CHAPTER V

DISCUSSIONS

5.1 The Binary Interaction Parameters of Selected Equations of State from Two Objective Functions

5.1.1 The Average Binary Interaction Parameters

Table 5.1 shows the average K_{ij} from fugacity and bubble point pressure method of all systems in this study. The average K_{ij} of any system at a given range of temperature is obtained by using every points of vapor-liquid equilibrium data sets. Due to the unknow value of the parameter η of the MPR equation of state, K_{ij} cannot be predicted.

From this table, the percent AAD from the bubble point pressure criterion are less than the percent AAD from the fugacity criterion in all cases. However, the computing time consumed by the bubble point pressure criterion is more than the computing time consumed by the fugacity criterion. This comparison is presented in Table 5.2 which systems containing CO_2 using the SRK equation of state are used as an example. The computing time requirement involved by the fugacity method is about seven times less than that used by the bubble point pressure method. The reason is that the fugacity method can avoid iterations in objective function calculations. Therefore, in weighing between these two methods, the accuracy must be sacrificed for the computing time and effort. For the computing time requirement, the average K_{ij} and percent AAD of all systems in this work are shown in Appendix C.

Another trend can be shown in Figures 5.1 and 5.2. Figure 5.1 shows the graphical depiction of the average K_{ij} values and carbon atom number of n-paraffin for systems containing methane and systems containing CO_2 using the SRK equation of state while Figure 5.2 shows the graphical depiction using the PR equation of state.

Table 5.1 The average binary interaction parameters and percent AAD for selected systems of five equations of state using fugacity and bubble point pressure criteria

SYSTEM	Range of T (K)	N		SRK EOS		PR EOS		PT EOS		MSRK EOS		MPR EOS	
				FUGA	BBP	FUGA	BBP	FUGA	BBP	FUGA	BBP	FUGA	BBP
Methane – Ethane	130.370–280.000	100	Kij	0.0028	−0.0028	0.0042	−0.0028	0.0000	−0.0056	−0.0014	−0.0014	0.0056	0.0014
			AAD(%)	2.1825	1.9778	2.0947	2.0480	2.6435	1.8602	1.7584	2.1919	1.6088	1.9334
Methane – Propane	144.260–213.710	62	Kij	0.0125	0.0094	0.0167	0.0177	0.0083	0.0073	0.0135	0.0104	0.0208	0.0208
			AAD(%)	2.4091	2.1052	2.3685	1.9352	2.1122	2.0286	2.7411	2.4495	1.4973	1.4973
Methane – n–Butane	166.493–283.160	76	Kij	0.0146	0.0115	0.0229	0.0188	0.0104	0.0063	0.0104	0.0083	0.0250	0.0229
			AAD(%)	3.7481	3.4016	3.5217	3.1406	3.7546	3.2543	5.0777	4.9090	3.1160	2.8964
Methane – Isobutane	310.938–344.271	31	Kij	0.0333	0.0319	0.0444	0.0306	0.0250	0.0194	−0.0236	−0.0264	0.0389	0.0385
			AAD(%)	1.7980	1.7253	2.1904	1.4244	1.7976	1.4967	1.1174	1.1004	1.8719	1.8708
Methane – n–Pentane	176.221–377.604	56	Kij	0.0111	0.0181	0.0292	0.0264	0.0056	0.0083	0.0028	0.0111	0.0222	0.0292
			AAD(%)	7.2292	6.6065	6.0848	6.2389	6.5261	6.3890	8.7050	8.1923	6.9431	5.9402
Methane – Isopentane	344.271–377.604	15	Kij	0.0236	0.0292	0.0319	0.0319	0.0083	0.0083	−0.0722	−0.0653	0.0250	0.0319
			AAD(%)	1.7880	1.5464	2.0025	2.0025	2.2560	2.2560	2.3453	2.0441	1.8933	1.3642
Methane – Neopentane	344.271–377.604	14	Kij	0.0514	0.0417	0.0611	0.0417	0.0417	0.0222	−0.0292	−0.0458	0.0375	0.0319
			AAD(%)	2.3630	2.1195	3.2210	2.4829	3.0297	2.5088	2.3922	1.9049	1.9094	1.9855
Methane – n–Hexane	190.510–273.170	64	Kij	0.0451	0.0458	0.0528	0.0521	0.0306	0.0299	0.0389	0.0389	0.0514	0.0514
			AAD(%)	2.2547	2.2406	2.4624	2.4306	2.8070	2.8260	3.7865	3.7865	2.9213	2.9213
Ethane – Propane	195.000–270.000	123	Kij	0.0052	0.0000	0.0042	−0.0021	0.0042	−0.0010	0.0052	0.0000	0.0063	0.0021
			AAD(%)	3.0091	2.5195	2.6506	1.7434	2.7126	2.0625	2.6198	1.9511	2.1908	1.6846
Ethane – n–Butane	338.716–366.493	10	Kij	0.0417	0.0326	0.0403	0.0306	0.0368	0.0292	0.0278	0.0243	0.0382	0.0306
			AAD(%)	1.7269	1.4564	4.8204	1.3646	1.6275	1.3836	1.2412	1.2236	1.5940	1.2610
Ethane – Isobutane	311.271–344.493	14	Kij	0.0115	−0.0156	0.0125	−0.0115	0.0094	−0.0146	0.0042	−0.0156	0.0135	−0.0083
			AAD(%)	4.0485	1.2064	3.8717	1.1578	3.6720	1.1504	3.3020	1.0343	3.5701	1.1965
Propane –Propylene	230.000–340.000	108	Kij	0.0094	0.0115	0.0094	0.0104	0.0104	0.0125	0.0104	0.0104		
			AAD(%)	1.3371	1.3569	0.6735	0.6497	0.8682	0.8386	0.5850	0.5850		
Propane – Isopentane	273.160–423.160	50	Kij	0.0031	0.0208	0.0042	−0.0042	0.0031	0.0073	0.0042	0.0000	0.0052	−0.0094
			AAD(%)	3.4264	3.7190	3.1214	4.6452	3.1666	2.6284	3.4486	3.7062	3.2235	6.0162

Table 5.1 (Continued)

SYSTEM	Range of T (K)	N		SRK EOS FUGA	SRK EOS BBP	PR EOS FUGA	PR EOS BBP	PT EOS FUGA	PT EOS BBP	MSRK EOS FUGA	MSRK EOS BBP	MPR EOS FUGA	MPR EOS BBP
Nitrogen – Methane	113.716–172.049	54	Kij	0.0306	0.0306	0.0347	0.0306	0.0333	0.0694	0.0306	0.0292	0.0514	0.1181
			AAD(%)	0.9053	0.9053	0.9214	0.8059	0.7901	6.6883	1.3909	0.8204	0.6941	13.8478
Nitrogen – Ethane	138.716–280.000	54	Kij	0.0437	0.0417	0.0583	0.0542	0.0479	0.0479	0.0354	0.0375	0.0792	0.0771
			AAD(%)	3.2333	3.3540	3.4963	3.6035	3.1901	3.1901	8.0019	7.8672	3.7808	3.8315
Nitrogen – Carbon dioxide	220.000–270.000	40	Kij	−0.0215	−0.0267	−0.0024	−0.0111	−0.0333	−0.0285	−0.1153	−0.0962	0.0514	0.0479
			AAD(%)	2.2007	2.2728	2.8103	2.6305	2.2204	2.2478	5.3097	5.1303	3.6122	3.6929
Carbon dioxide – Methane	219.260–270.000	43	Kij	0.1056	0.0986	0.1056	0.0986	0.1000	0.0958	0.0958	0.0889	0.1181	0.1069
			AAD(%)	2.3700	1.7179	4.3576	2.1644	2.9962	1.8639	2.8174	2.3729	3.9571	3.1708
Carbon dioxide – Ethane	250.000	13	Kij	0.1292	0.1347	0.1250	0.1319	0.1306	0.1375	0.1319	0.1403	0.1236	0.1319
			AAD(%)	0.9351	0.4264	1.1774	0.4237	1.0997	0.4218	1.3370	0.4893	1.5256	0.6448
Carbon dioxide – Propane	244.271–266.493	21	Kij	0.1319	0.1347	0.1264	0.1292	0.1306	0.1333	0.1250	0.1361	0.1250	0.1292
			AAD(%)	1.9771	2.0059	1.8160	1.8643	1.8111	1.8022	2.1313	1.8871	2.1313	2.1004
Carbon dioxide – n–Butane	368.160–393.160	13	Kij	0.1917	0.1653	0.1750	0.1500	0.1806	0.1569	0.1833	0.1611	0.1764	0.1542
			AAD(%)	2.3485	0.7164	2.2359	0.5666	2.1302	0.5645	1.6878	0.6284	1.9221	0.6088
Carbon dioxide – i–Butane	310.938–344.271	14	Kij	0.1417	0.1347	0.1306	0.1250	0.1333	0.1500	0.1389	0.1347	0.1306	0.1292
			AAD(%)	1.9446	1.8320	1.7120	0.6740	1.7459	3.5407	1.8024	1.8031	1.9507	1.9522
Carbon dioxide – n–Pentane	277.660–438.160	54	Kij	0.1583	0.1403	0.1486	0.1319	0.1486	0.1319	0.1528	0.1389	0.1500	0.1319
			AAD(%)	5.1257	3.9798	5.2274	3.7125	5.1432	3.7183	4.7270	3.6789	5.3676	3.7061
Carbon dioxide – i–Pentane	408.160	9	Kij	0.2236	0.1694	0.1986	0.1500	0.2014	0.1528	0.2083	0.1542	0.2014	0.1528
			AAD(%)	5.1059	1.2176	4.8516	1.2907	4.7978	1.4259	4.9727	1.7084	4.8375	1.3493
Carbon dioxide – n–Heptane	310.660–477.216	45	Kij	0.1167	0.1125	0.1097	0.1000	0.1014	0.0917	0.1111	0.1069		
			AAD(%)	2.5043	2.1455	3.7464	2.6949	3.9968	2.9486	3.3983	3.1278		
Carbon dioxide – n–Decane	462.560–583.660	16	Kij	0.1472	0.1500	0.1194	0.1167	0.0778	0.0722	0.1111	0.1056		
			AAD(%)	3.6182	3.7719	3.1596	2.9978	2.8798	2.4923	1.9101	1.6407		

The 5.2 The computing time of the average Kij calculation required by both criteria for systems containing CO2 with the SRK equation of state

System	Range of T (K)	N	Computing time (min. : sec.)	
			FUGA	BBP
Carbon dioxide - Methane	219.260-270.000	43	00:10	01:42
Carbon dioxide - Ethane	250.000	13	00:06	00:50
Carbon dioxide - Propane	244.271-266.493	21	00:12	00:56
Carbon dioxide - n-Butane	368.160-393.160	13	00:06	00:50
Carbon dioxide - i-Butane	310.938-344.271	14	00:07	00:51
Carbon dioxide - n-Pentane	277.660-438.160	54	00:17	01:56
Carbon dioxide - i-Pentane	408.160	9	00:04	00:34
Carbon dioxide - n-Heptane	310.660-477.216	45	00:10	01:50
Carbon dioxide - n-Decane	462.560-583.660	16	00:09	00:53

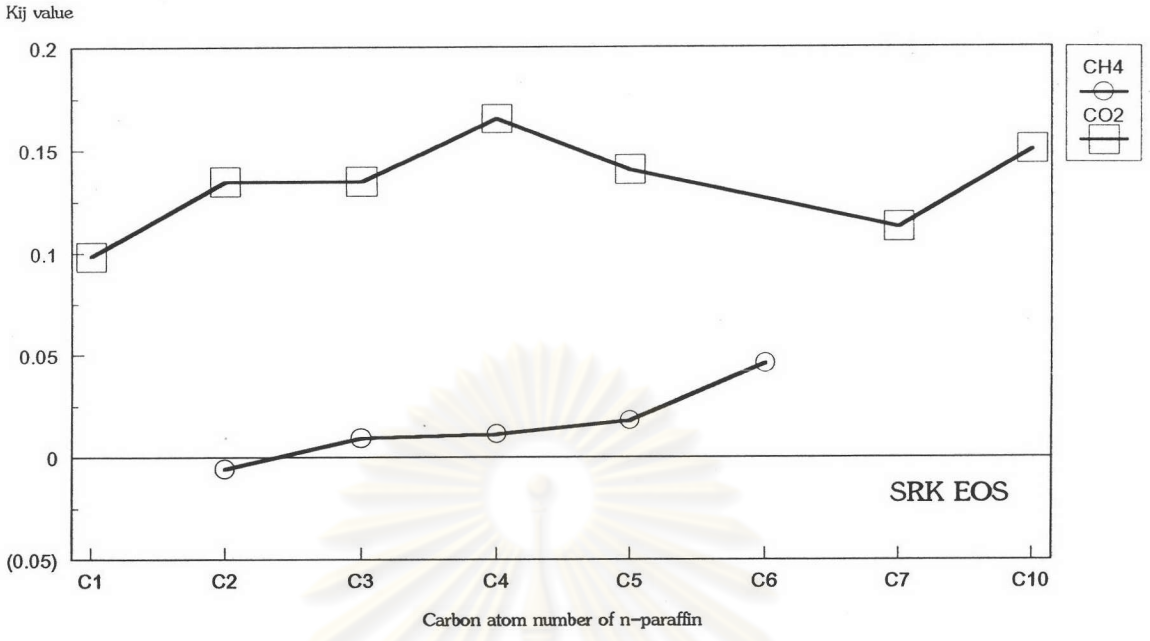


Figure 5.1 The graphical depiction of the average Kij values and carbon atom number of n-paraffin for systems containing methane and systems containing CO_2 using the SRK equation of state

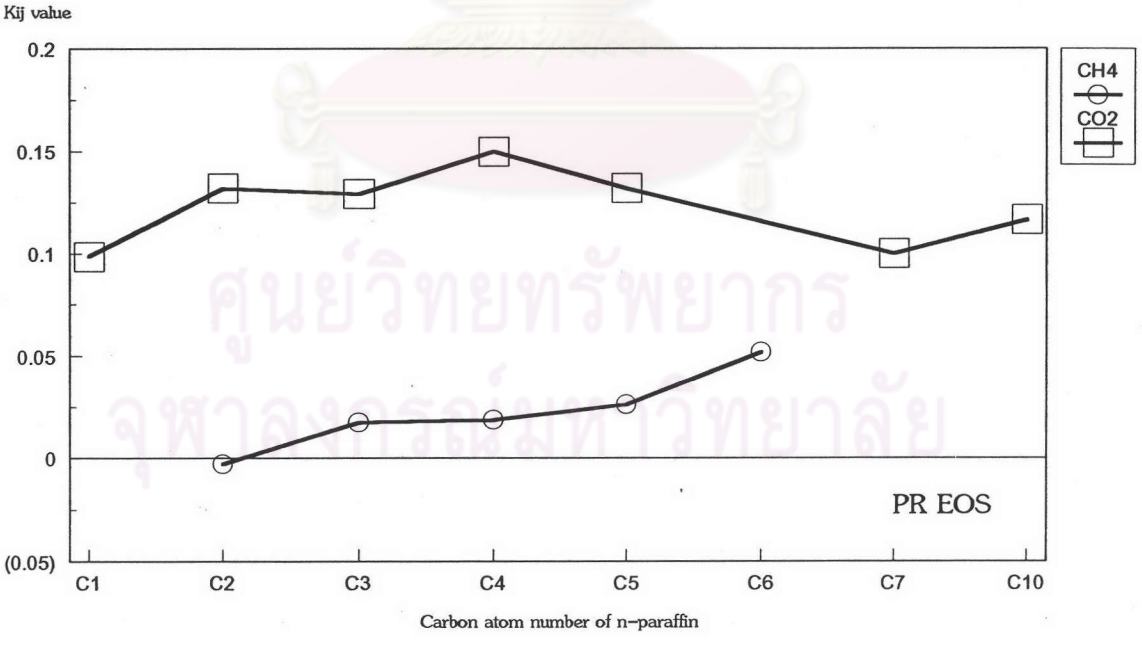


Figure 5.2 The graphical depiction of the average Kij values and carbon atom number of n-paraffin for systems containing methane and systems containing CO_2 using the PR equation of state

5.1.2 Systems Containing Methane

The average K_{ij} values of methane systems from two criteria are shown in Table 5.1. From this table, most of the percent AAD are less than 5.0 % except the methane - n-pentane system. The K_{ij} values were found to be close to zero for the methane - ethane system and less than 0.05 for the methane - heavier hydrocarbon systems. Morever, some K_{ij} values are negative, especially for some systems using the MSRK equation of state.

For two objective functions, K_{ij} values are almost equal but the percent AAD from bubble point pressure method are 1.1 less than the percent AAD from fugacity method. The differences in K_{ij} values of the two methods are less than 0.01 for SRK and MPR, 0.02 for PR, PT, and MSRK. The statistical relationship of the K_{ij} values from both methods can be demonstrated in regression which the degree of relation between two data sets may be measured by the alue of R^2. For systems containing methane using five equations of state, all of the relationships are in the acceptable range with the slope m and R^2 in range of 0.8982-1.072 and 0.7221-0.8952 respectively as shown in Figure 5.3.

An important observation from this relationship is that when the fugacity criterion is applied to find the optimum K_{ij} for a given EOS, the procedure is independent of the accuracy with which the value of bubble pressure, composition or any other equilibrium variables are predicted. This is because all P-T-x-y data are introduced into the objective function of fugacity method whereas only P-T-x data are used in the bubble point pressure method. Therefore, this reason may explain why the accuracy of the K_{ij} predicted by fugacity criterion is less than that predicted by the bubble point pressure criterion.

5.1.3 Systems Containing Ethane and Systems Containing Propane

Using fugacity and bubble point pressure method, the optimum K_{ij} values of ethane systems are shown in Table 5.1. The K_{ij} of ethane systems are close to zero for only ethane - propane system. All percent AAD are within the limit of 5.0 %.

The percents AAD from bubble point pressure method are less than the percents AAD from the fugacity method as shown in Table 5.1. The differences in K_{ij} values of fugacity and bubble point pressure method are less than 0.03 for most cases. The relationship of K_{ij} from two criteria are shown in Figure 5.4. The slope m and R^2 from all equations are in the range of 0.6902 - 0.7996 and 0.9387 - 0.1484 respectively.

The average K_{ij} for two propane systems -- propane-propylene system and propane - isopentane system are shown in Table 5.1 From this table, K_{ij} values and percent AAD are less than 0.021 and 5.0 respectively in all cases.

For both criteria, the percents AAD from the bubble point pressure method are still less than the percents AAD from fugacity method. The differences in K_{ij} values of two criteria do not exceed the limit of 0.02. The K_{ij} relationship from two criteria are shown in Figure 5.5. The slope m and R^2 are in range of 0.8831 - 1.0480 and 0.7007 - 0.8405 respectively. It can be seen that the PR and MSRK equations give higher values of R^2 than the other equations of state.

5.1.4 Systems Containing Nitrogen

The average K_{ij} values from two criteria for nitrogen systems are shown in Table 5.1. From this Table, almost all values of K_{ij} are higher than 0.03 except the K_{ij} for the nitrogen-carbon dioxide system using SRK, PR, PT and MSRK equations of state which are negative. It should be noted that the average K_{ij} for nitrogen - carbon dioxide system are negative because of non-hydrocarbon - non-hydrocarbon system. It is also found that the K_{ij} for systems containing non-hydrocarbon are higher than the K_{ij} for hydrocarbon- hydrocarbon system

For comparison of the K_{ij} from the bubble point pressure method and from the fugacity method , the differences of K_{ij} values from both criteria are less than 0.01. And when the regression of the K_{ij} values from both criteria are shown in Figure 5.6, the slope m and R^2 are in the acceptable range of 0.9046 - 1.1866 and 0.8588 - 0.9650 respectively.

5.1.5 Systems Containing Carbon Dioxide

The K_{ij} values of systems containing carbon dioxide are presented in Table 5.1. Most of the K_{ij} values are in the range of 0.1 - 0.2. The influence of the molecular weight is significant in these systems. For CO_2 - hydrocarbon systems, the K_{ij} values increase with the molecular weight of hydrocarbon components for C_1 - C_4.

The results from two criteria -- the bubble point pressure method and the fugacity method are almost equal. The differences of K_{ij} from both criteria is less than 0.02 for binary systems containing methane or ethane or propane and less than 0.06 for binary systems containing butane, pentane, heptane, or n-decane. The AAD(%) from the bubble point pressure method are still less than that from the fugacity method, especially, the systems containing high molcular weight hydrocarbon. The AAD(%) from the bubble point pressure method and the fugacity method for all systems are in the range of 0.42 - 4.0 % and 0.92 - 5.4 % respectively. The regression of the K_{ij} values from both methods was done using all five equations and the result of each equation is presented in Figure 5.7. The result of this analysis yields R squared of 0.78 for the MPR equation and over 0.85 for the SRK , PR, PT and MSRK equations whereas the slopes, m in all equations are close to unity.

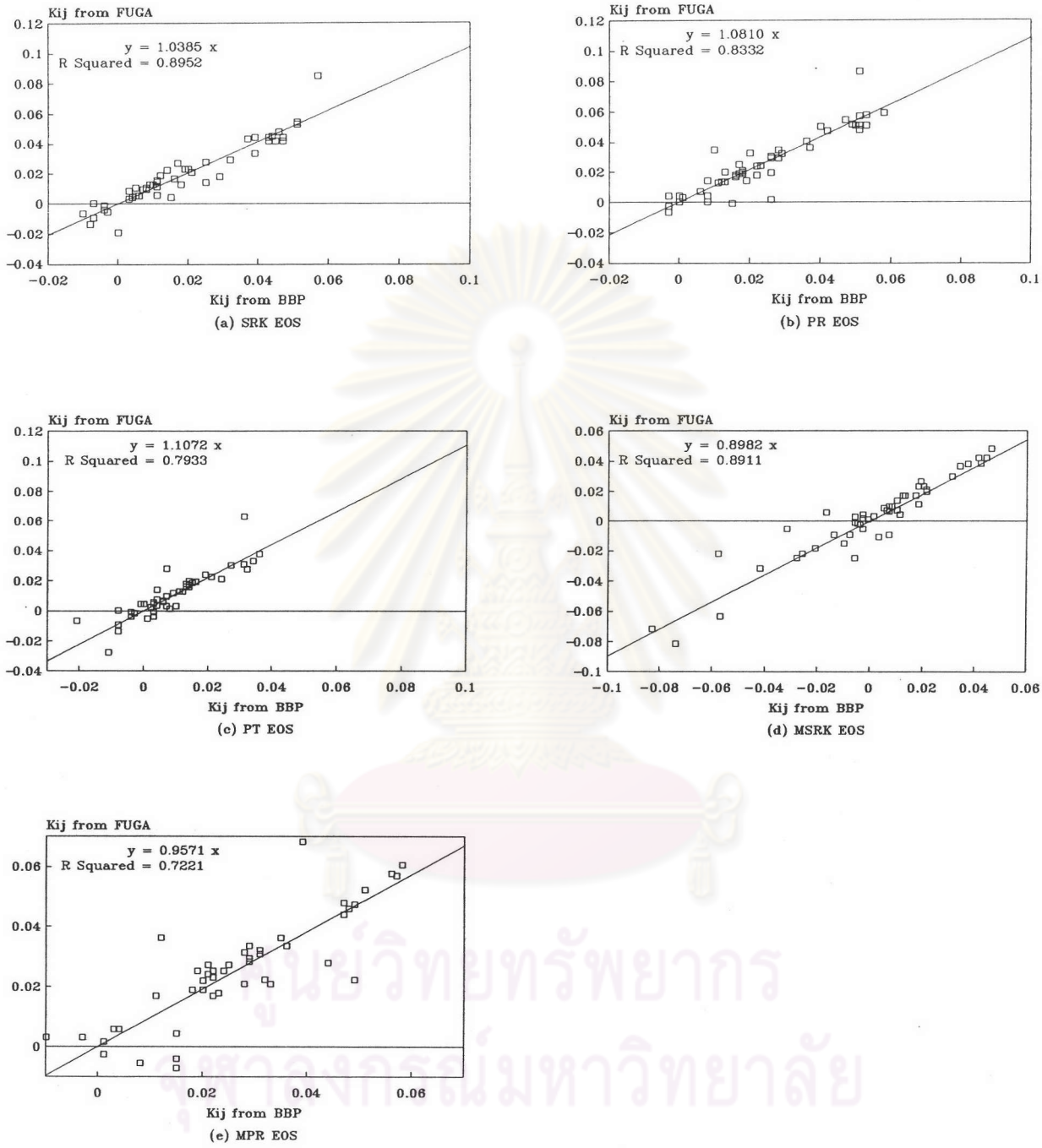


Figure 5.3 Regression results of the optimum Kij values calculated by both criteria for systems containing methane using five equations of state, (a) SRK, (b) PR, (c) PT, (d) MSRK (e) MPR

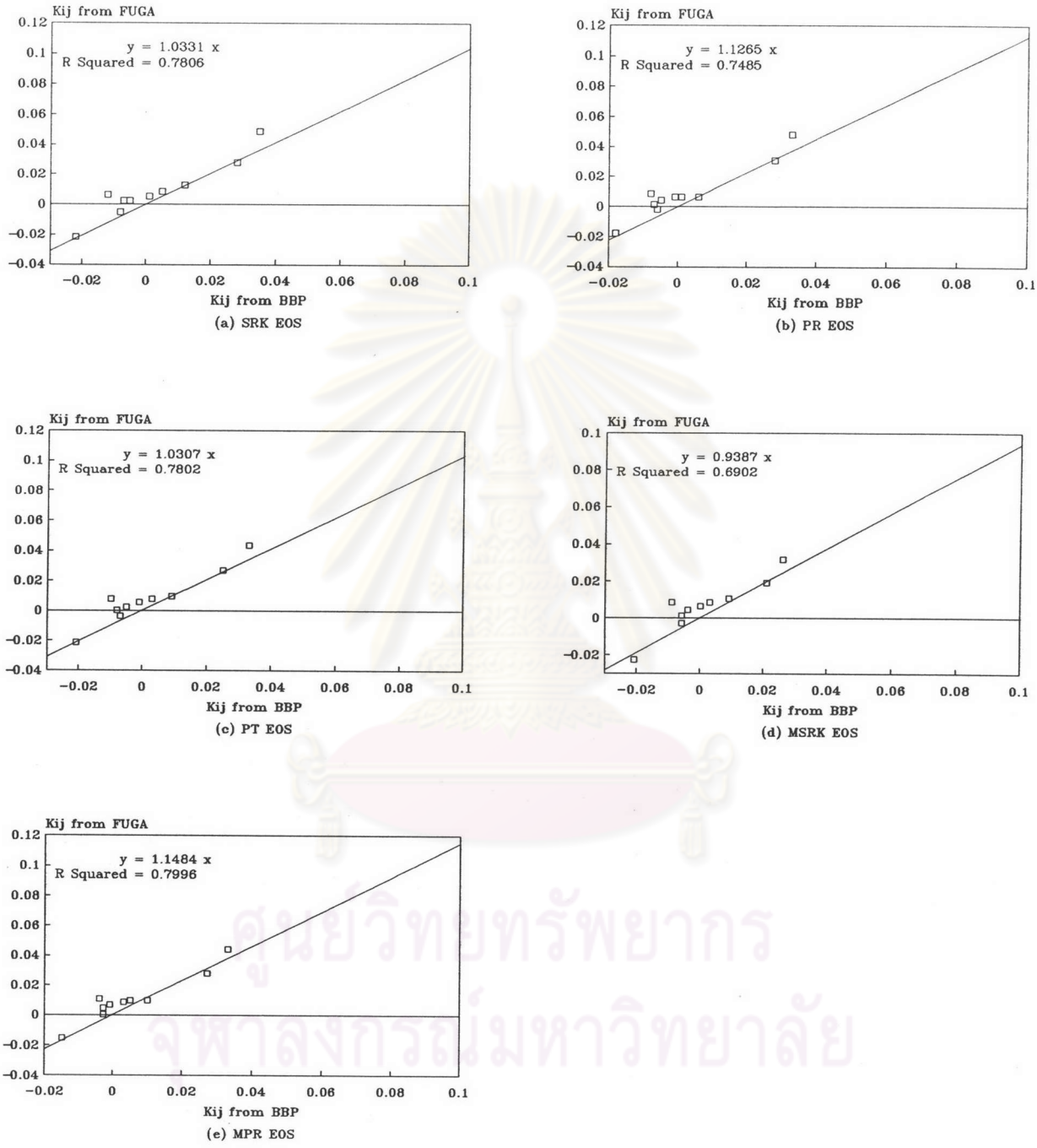


Figure 5.4 Regression results of the optimum Kij values calculated by both criteria for systems containing ethane using five equations of state, (a) SRK, (b) PR, (c) PT, (d) MSRK, (e) MPR

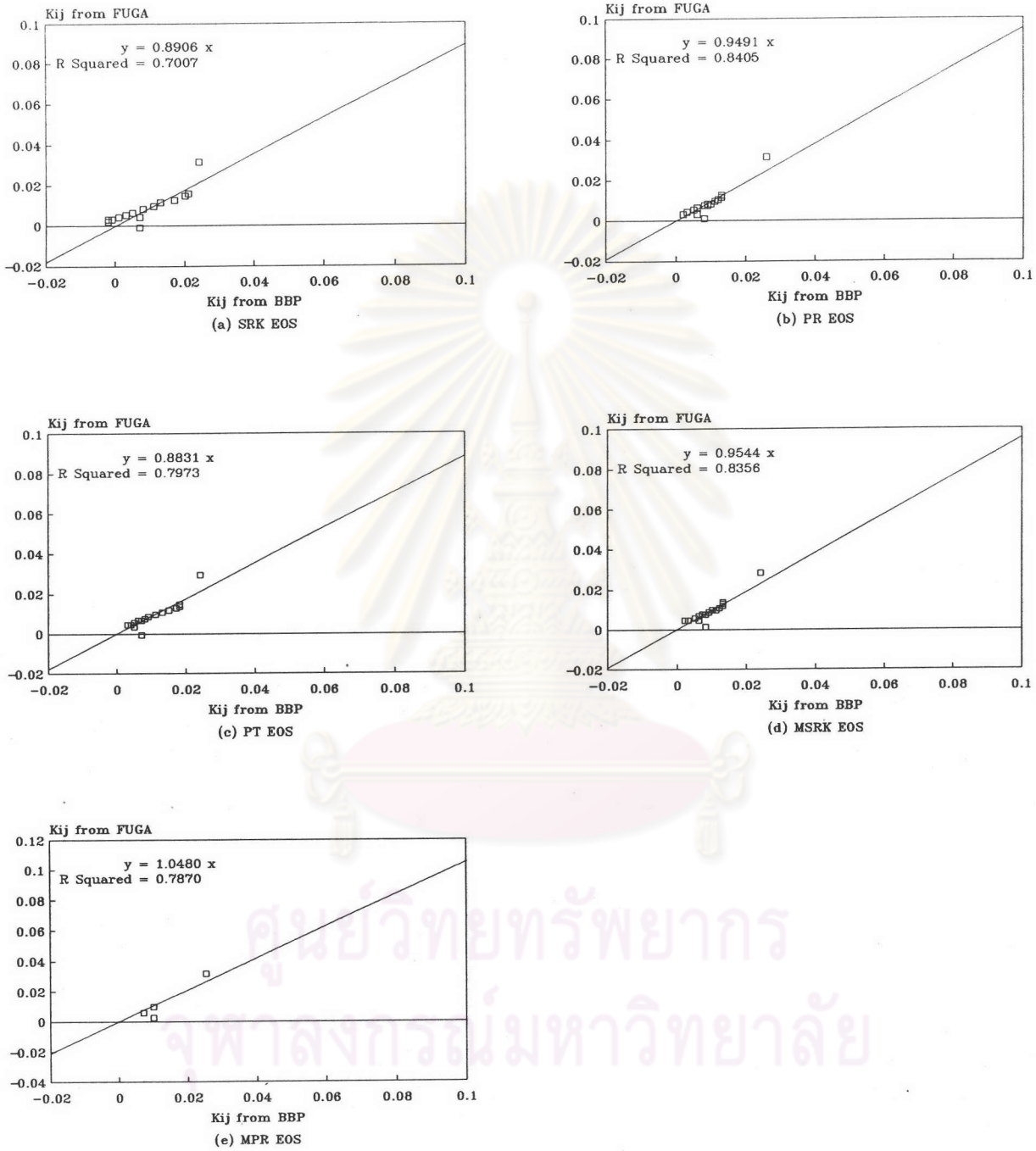
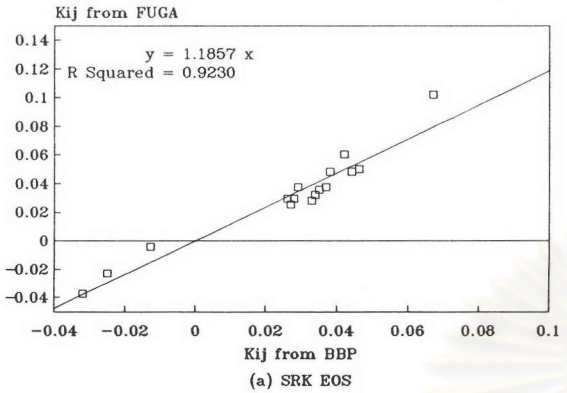
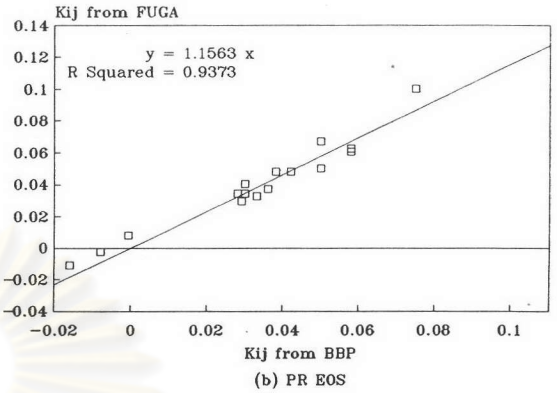
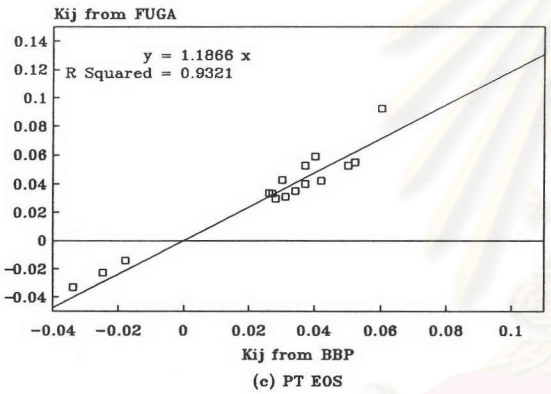
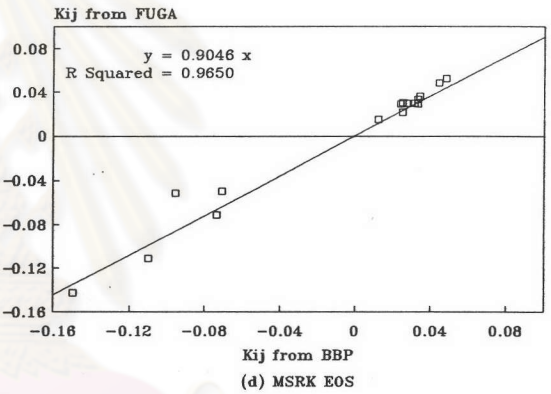


Figure 5.5 Regression results of the optimum Kij values calculated by both criteria for systems containing propane using five equations of state, (a) SRK, (b) PR, (c) PT, (d) MSRK, (e) MPR









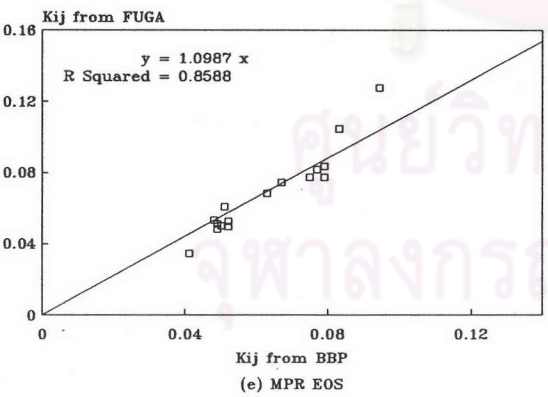


Figure 5.6 Regression results of the optimum Kij values calculated by both criteria for systems containing nitrogen using five equations of state, (a) SRK, (b) PR, (c) PT, (d) MSRK, (e) MPR

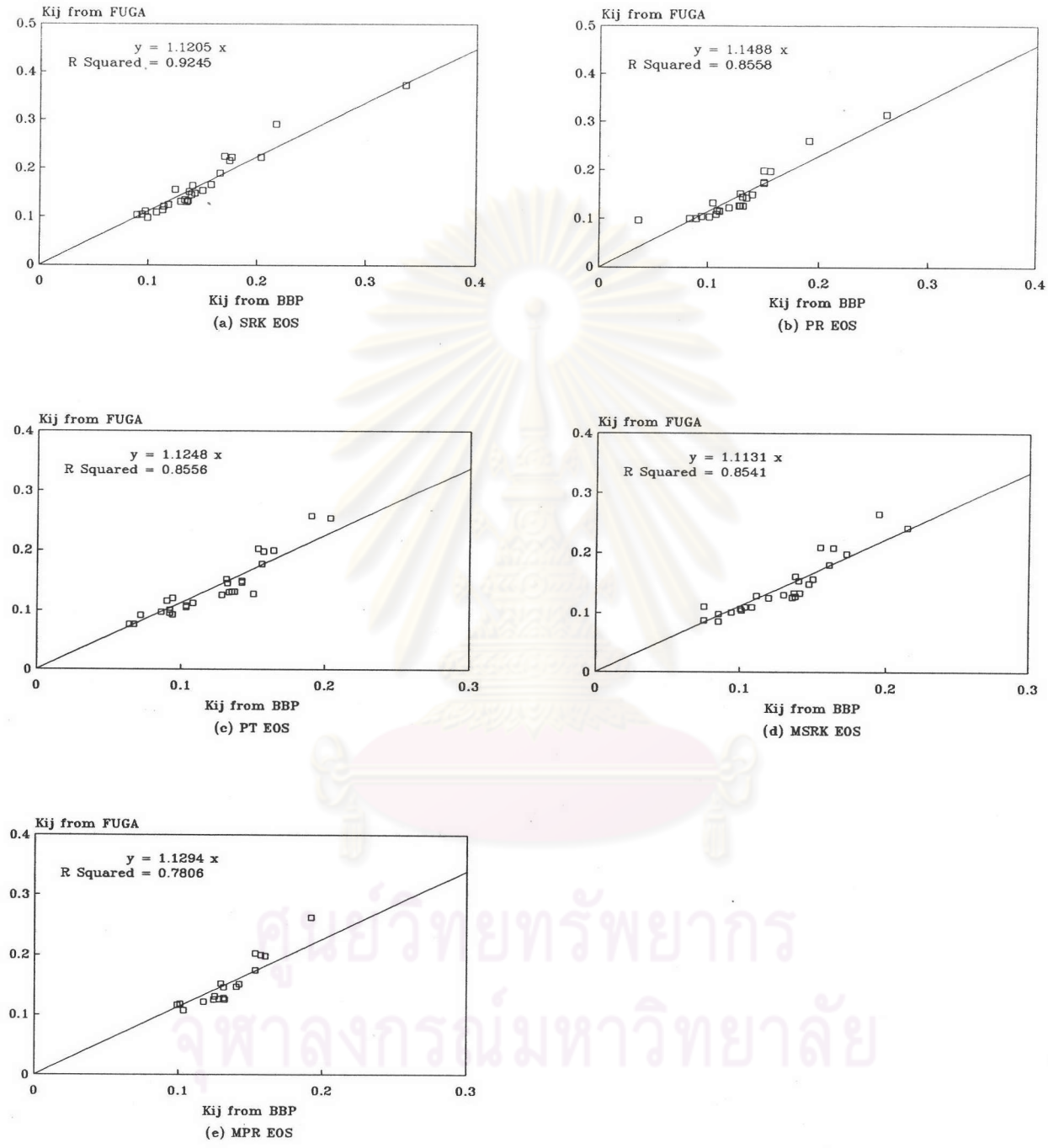


Figure 5.7 Regression results of the optimum Kij values calculated by both criteria for systems containing carbon dioxide using five equations of state, (a) SRK, (b) PR, (c) PT, (d) MSRK, (e) MPR

5.2 Significance of Binary Interaction Parameters in Vapor-Liquid Equilibrium Calculations

The absolute average percent deviation (AAD) in predicted bubble point pressures using five equations of state with and without K_{ij} are given in Table 5.3 for methane systems, Table 5.4 for ethane systems, Table 5.5 for propane systems, Table 5.6 for nitrogen and Table 5.7 for CO_2 systems. In these tables, the average K_{ij} from bubble point pressure method (Table 5.1) are used.

Evidently, the incorporation of the optimum K_{ij} into the mixing rules of each equation of state increases the accuracy of the predicted bubble pressure values, especially for the CO_2 - hydrocarbon, N_2 - hydrocarbon and hydrocarbon - high molecular weigh hydrocarbon systems. The percent AAD between the experimental and predicted values of every pair decrease dramatically from over 10% to less than 4% in these systems.

As an example of the accuracy improvement, Figure 5.8 gives the comparison of the VLE calculation of CO_2 - methane, CO_2 - ethane, CO_2 - propane, CO_2 - n-butane and CO_2 - n-pentane systems at two different temperatures with and without the optimum K_{ij} using PT equation of state.

Therefore, for systems containing CO_2, N_2 and high molecular weight hydrocarbon which the K_{ij} values are over 0.03, this coefficient cannot be neglected in performing the VLE calculations no matter which equation is used.

For other hydrocarbon - hydrocarbon systems, since the K_{ij} values are less than those in CO_2 , N_2 and high molecular weight mixtures, their effect in the VLE prediction accuracy is not so meaningful, especially for methane - light hydrocarbon binaries at low to medium temperatures.

Table 5.3 Comparison of percent AAD with and without Kij for systems containing methane using five equations of state

SYSTEM	T (K)	Range of P (atm)	N	SRK EOS AAD(%) (with Kij)	SRK EOS AAD(%) (Kij=0)	PR EOS AAD(%) (with Kij)	PR EOS AAD(%) (Kij=0)	PT EOS AAD(%) (with Kij)	PT EOS AAD(%) (Kij=0)	MSRK EOS AAD(%) (with Kij)	MSRK EOS AAD(%) (Kij=0)	MPR EOS AAD(%) (with Kij)	MPR EOS AAD(%) (Kij=0)
Methane – Ethane				Kij=−0.0028		Kij=−0.0028		Kij=−0.0056		Kij=−0.0014		Kij=0.0014	
	130.370	1.9053–3.3070	4	2.8282	2.2003	2.6764	2.2088	2.7209	1.6416	2.3613	2.0644	1.7003	2.0167
	144.260	1.8577–6.6685	7	2.7719	1.7644	3.7575	2.7131	3.3959	1.3759	2.9483	2.3863	1.7097	2.3071
	158.150	1.7556–13.5412	10	2.6392	3.1899	2.3121	2.5324	2.4603	3.3774	2.3584	2.5185	2.5713	2.4850
	172.040	2.0958–23.1016	9	1.3565	1.6996	1.3444	1.0973	1.1197	1.6874	1.8720	1.1873	0.9451	1.1664
	186.110	2.4973–35.6561	8	0.8781	1.3384	1.3116	1.0062	0.9645	1.4439	1.0889	1.3184	1.1950	1.4549
	189.650	2.4360–41.8483	10	2.4553	1.5303	1.2328	1.0623	1.0846	1.6689	3.0110	3.7217	1.1027	4.6236
	190.940	2.6878–45.4547	10	3.8310	6.3910	5.3922	6.3342	4.3744	10.6881	5.3610	22.0358	7.3821	8.1749
	192.390	2.6538–40.8276	8	1.4533	2.1774	1.0041	1.0759	1.1084	2.3061	1.9531	2.3340	0.8632	0.9790
	199.920	3.0621–40.8276	8	1.5235	2.2482	1.3087	1.3293	1.3575	2.3514	2.4333	2.8066	0.9224	0.9630
	260.000	17.8000–55.1800	10	1.0683	0.9730	1.1935	0.9392	1.0368	0.7439	1.4603	1.6131	1.0514	1.2063
	270.000	22.5300–50.2600	9	1.7218	1.5428	1.9535	1.7273	1.8513	1.4207	0.5988	0.7185	1.6601	1.7707
	280.000	28.5000–46.5000	7	1.2260	1.1800	1.1158	1.0199	1.0882	0.9324	1.1742	5.0799	0.8868	4.8206
	130.370–280.000	1.858–55.180	100	1.9778	2.2555	2.0480	1.9636	1.8602	2.6435	2.1919	4.2824	1.9334	2.7647
Methane – Propane				Kij=0.0094		Kij=0.0177		Kij=0.0073		Kij=0.0104		Kij=0.0208	
	144.260	2.1094–7.3490	6	2.7551	4.7543	2.4752	5.9117	2.6955	3.7877	2.8610	5.1778	2.6512	6.5752
	158.150	1.7011–13.7113	8	3.3822	6.0532	2.1680	7.4580	3.1396	5.2530	3.2198	6.3108	1.4371	7.9835
	172.040	2.0958–23.2717	8	2.0736	4.6306	1.2619	6.4141	1.6579	3.6869	1.9888	4.9797	0.7349	7.0712
	187.540	2.7899–39.8750	9	1.3562	2.7748	1.3291	4.4024	1.3828	19.8804	1.3497	3.0014	1.2987	9.3957
	192.300	2.0414–39.1264	9	1.8541	2.9909	2.1802	5.7505	1.8882	1.7905	1.9908	3.1992	1.3654	7.9655
	195.200	2.0754–44.2299	11	1.4824	3.3644	1.5549	5.5053	1.3857	2.3802	1.6033	3.4281	1.4737	7.3914
	213.710	1.8713–61.2414	11	2.2860	2.3683	2.6369	4.3544	2.4127	1.3641	4.1211	2.0269	1.7602	6.7746
	144.260–213.710	1.701–44.230	62	2.1052	3.6927	1.9352	5.5852	2.0286	5.3301	2.4495	3.8258	1.4973	7.6123
Methane – n–Butane				Kij=0.0115		Kij=0.0188		Kij=0.0063		Kij=0.0083		Kij=0.0229	
	166.493	1.3609–19.2570	8	3.6998	8.4312	3.1258	11.0713	3.9547	6.5884	5.0898	8.5926	1.4844	11.1369
	177.604	1.3609–29.4906	8	2.7731	7.0230	2.3973	9.7761	2.6343	5.1010	3.7947	7.0365	1.0343	9.9741
	185.938	1.3609–37.3573	9	3.5330	7.3712	3.3816	10.2543	3.3153	5.4884	4.4834	7.2852	2.8109	10.9686
	194.104	1.3609–46.0671	10	3.0533	8.5750	2.7074	7.5638	2.5602	2.6557	2.8573	4.8008	2.9909	8.6623
	199.893	13.6160–51.0345	7	2.9837	3.9788	2.5585	6.5478	2.2875	2.3685	2.8356	3.7867	2.6611	7.8110
	210.938	1.3609–54.3007	9	5.0245	2.4452	4.4373	6.1589	5.3131	2.0928	5.1675	2.1495	3.4818	8.5357
	227.560	3.4000–81.4400	8	4.4012	4.4496	4.4868	6.3378	4.0563	3.3969	5.9149	4.8240	4.4374	8.8161
	255.360	1.3600–108.6600	8	3.7766	4.9522	3.9935	6.7732	3.1845	3.1736	8.2138	4.9961	5.1250	9.4887
	283.160	3.4703–95.2644	9	1.4309	3.1001	1.2564	5.0524	1.9350	1.7761	5.6856	5.7512	2.0336	7.8678
	166.493–283.160	1.360–108.660	76	3.4016	5.6408	3.1406	7.7149	3.2543	3.5978	4.9090	5.4576	2.8964	9.2497

Table 5.3 (Continued)

SYSTEM	T (K)	Range of P (atm)	N	SRK EOS AAD(%) (with Kij)	SRK EOS AAD(%) (Kij=0)	PR EOS AAD(%) (with Kij)	PR EOS AAD(%) (Kij=0)	PT EOS AAD(%) (with Kij)	PT EOS AAD(%) (Kij=0)	MSRK EOS AAD(%) (with Kij)	MSRK EOS AAD(%) (Kij=0)	MPR EOS AAD(%) (with Kij)	MPR EOS AAD(%) (Kij=0)
Methane – Isobutane				Kij=0.0319		Kij=0.0306		Kij=0.0194		Kij=−0.0264		Kij=0.0385	
	310.938	5.4437–108.8736	18	1.3201	4.0630	0.5582	4.9516	1.1533	2.3022	1.0780	4.4300	1.5599	5.8173
	344.271	13.6092–95.2644	13	2.2862	5.8394	2.6238	6.3312	1.9721	4.2519	1.1314	3.1074	2.3012	5.7517
	310.938–344.271	5.444–108.874	31	1.7253	4.8080	1.4244	5.5301	1.4967	3.1198	1.1004	3.8754	1.8708	5.7898
Methane – n–Pentane				Kij=0.0181		Kij=0.0264		Kij=0.0083		Kij=0.0111		Kij=0.0292	
	176.221	1.3677–20.4274	6	9.4965	20.5468	8.3788	24.6798	10.5124	15.7716	13.8898	20.5324	5.2480	23.8382
	192.638	6.8182–40.8276	4	5.8918	12.3016	5.7153	16.5882	6.4925	8.2241	7.2221	12.0157	5.3575	17.1142
	194.182	6.8114–40.8276	4	6.0824	11.0077	6.1127	15.4361	6.4506	6.6555	5.6279	10.6526	6.2863	16.0970
	199.871	3.4159–40.8276	5	7.6975	7.7845	7.6714	12.6428	7.9992	6.2869	6.4458	7.1423	7.8138	13.8014
	223.932	6.8182–81.6552	7	9.8263	7.5682	9.7947	8.4655	10.2666	8.1076	9.2282	7.1958	8.6835	9.5635
	248.349	6.8182–112.4828	10	4.0190	6.6308	4.1066	9.9331	4.1977	4.2469	4.7378	3.9163	4.0794	13.4219
	273.171	13.6228–136.0920	10	7.3611	11.3058	6.8005	13.3647	7.0348	8.3337	5.2631	6.2968	8.8999	16.7553
	377.604	68.1140–136.0240	10	4.4016	6.9593	3.5805	7.6989	1.8752	3.0890	12.7193	10.8791	2.4941	6.3348
	176.221–377.604	1.368–136.092	56	6.6065	9.9531	6.2389	12.6539	6.389	7.1256	8.1923	9.1227	5.9402	13.874
Methane – Isopentane				Kij=0.0292		Kij=0.0319		Kij=0.0083		Kij=−0.0653		Kij=0.0319	
	344.271	34.1591–149.0888	8	1.3508	4.5602	1.6031	5.7666	2.0502	2.3166	1.5880	10.4172	1.1302	5.6570
	377.604	33.9550–129.2194	7	1.7700	5.1254	2.4589	6.0964	2.4911	2.7425	2.5655	11.0941	1.6317	4.4434
	344.271–377.604	33.955–149.089	15	1.5464	4.824	2.0025	5.9205	2.256	2.5154	2.0441	10.7331	1.3642	5.0907
Methane – Neopentane				Kij=0.0417		Kij=0.0417		Kij=0.0222		Kij=−0.0458		Kij=0.0319	
	344.271	21.0943–118.9444	9	1.6425	5.4861	2.1914	6.3129	2.2671	3.8419	1.8655	6.1213	2.0091	4.4814
	377.604	20.9582–85.1255	5	2.9781	5.4889	3.0077	5.4945	2.9437	3.8858	1.9758	5.7405	1.9430	3.8771
	344.271–377.604	20.958–118.944		2.1195	5.4871	2.4829	6.0206	2.5088	3.8576	1.9049	5.9853	1.9855	4.2655
Methane – n–Hexane				Kij=0.0458		Kij=0.0521		Kij=0.0299		Kij=0.0389		Kij=0.0514	
	190.510	1.3609–33.9958	5	2.1749	27.3770	2.1912	31.1188	2.7121	20.8114	3.5140	26.0776	2.9118	25.0579
	193.160	1.3677–34.0298	5	2.9097	26.3010	2.9274	30.1449	3.4233	19.5577	3.1672	24.9434	3.5725	28.2495
	198.060	1.3541–40.8276	10	1.2988	25.1510	1.3240	29.0544	1.3573	18.5581	1.7961	23.6566	2.9359	27.5360
	210.160	1.3745–40.8276	9	3.2828	26.5345	3.5757	30.4126	3.7857	19.8455	4.8029	24.6644	3.0988	29.7384
	223.160	1.3745–68.0460	11	2.6205	21.2449	2.6109	25.1787	2.7487	14.1370	2.5764	18.4604	2.7275	25.2730
	248.150	1.3677–68.0460	11	2.4912	19.4068	2.9601	23.0167	2.0101	12.0592	2.5355	14.6537	3.3334	24.1307
	273.170	1.7080–108.8736	13	1.4780	15.4364	1.7894	18.4738	3.8611	7.9318	7.0395	7.8683	2.3556	20.2741
	190.510–273.170	1.354–108.874	64	2.2406	21.9774	2.4306	25.6388	2.8260	14.9579	3.7865	18.4405	2.9213	25.5710

Table 5.4 Comparison of percent AAD with and without Kij for systems containing ethane using five equations of state

SYSTEM	T (K)	Range of P (atm)	N	SRK EOS AAD(%) (with Kij)	SRK EOS AAD(%) (Kij=0)	PR EOS AAD(%) (with Kij)	PR EOS AAD(%) (Kij=0)	PT EOS AAD(%) (with Kij)	PT EOS AAD(%) (Kij=0)	MSRK EOS AAD(%) (with Kij)	MSRK EOS AAD(%) (Kij=0)	MPR EOS AAD(%) (with Kij)	MPR EOS AAD(%) (Kij=0)
Ethane – Propane				Kij=0.0000		Kij=−0.0021		Kij=−0.0010		Kij=0.0000		Kij=0.0021	
	195.000	0.2981–1.5623	15	4.9179	4.9179	3.5796	3.1306	3.8832	3.6115	3.7137	3.7137	3.5138	4.1479
	210.000	0.5073–2.8285	18	2.0356	2.0356	1.8094	1.4336	1.7498	1.5424	1.7016	1.7016	1.6654	2.0949
	225.000	0.7718–3.5529	18	1.6353	1.6353	1.1279	1.0653	1.3558	1.3242	1.1962	1.1962	1.1314	1.3517
	235.000	2.0183–7.1345	18	2.8215	2.8215	2.2589	2.5729	2.5346	2.6892	2.2810	2.2810	1.9005	1.5913
	245.000	2.2897–6.5295	18	1.5792	1.5792	0.9127	1.5249	1.2987	1.6050	1.2764	1.2764	0.9282	0.5085
	255.000	3.5865–9.2642	18	2.4463	2.4463	1.3144	1.9175	1.9121	2.2100	1.8060	1.8060	1.4153	0.8149
	270.000	4.8951–14.1683	18	2.6007	2.6007	1.5069	1.9607	2.0066	2.2304	1.9765	1.9765	1.5422	1.1070
	195.000–270.000	0.298–14.168	123	2.5195	2.5195	1.7434	1.9147	2.0625	2.1381	1.9511	1.9511	1.6846	1.5988
Ethane – n–Butane				Kij=0.0326		Kij=0.0306		Kij=0.0292		Kij=0.0243		Kij=0.0306	
	338.716	34.9756–47.7002	4	1.6879	4.2772	1.5766	4.4721	1.6660	4.1105	1.4551	3.3110	1.5125	4.3901
	366.493	34.6354–47.0198	6	1.3021	5.2455	1.2232	5.2686	1.1954	4.8458	1.0693	3.8707	1.0933	5.1334
	338.716–366.493	34.635–47.700	10	1.4564	4.8582	1.3646	4.9500	1.3836	4.5517	1.2236	3.6468	1.2610	4.8361
Ethane – Isobutane				Kij=−0.0156		Kij=−0.0115		Kij=−0.0146		Kij=−0.0156		Kij= -0.0083	
	311.271	10.5471–39.8069	7	1.0407	3.6055	1.0690	3.0694	0.9867	3.4766	0.9953	3.5603	1.0776	2.5299
	311.271	10.5471–39.8069	7	1.0407	3.6055	1.0690	3.0694	0.9867	3.4766	0.9953	3.5603	1.0776	2.5299

Table 5.5 Comparison of percent AAD with and without Kij for systems containing propane using five equations of state

SYSTEM	T (K)	Range of P (atm)	N	SRK EOS AAD(%) (with Kij)	SRK EOS AAD(%) (Kij=0)	PR EOS AAD(%) (with Kij)	PR EOS AAD(%) (Kij=0)	PT EOS AAD(%) (with Kij)	PT EOS AAD(%) (Kij=0)	MSRK EOS AAD(%) (with Kij)	MSRK EOS AAD(%) (Kij=0)	MPR EOS AAD(%) (with Kij)	MPR EOS AAD(%) (Kij=0)
				Kij=0.0115		Kij=0.0104		Kij=0.0125		Kij=0.0104			
Propane –Propylene	230.000	0.9968–1.2139	9	2.4708	5.0241	0.7967	3.1252	1.3208	4.1877	0.7897	3.1433		
	240.000	1.5199–1.8357	9	1.9146	4.3125	0.8965	3.1291	1.2264	3.9110	0.8110	3.0096		
	250.000	2.2403–2.6746	9	1.2183	3.4770	0.7478	2.8830	0.9134	3.4379	0.6309	2.6937		
	260.000	3.1779–3.7789	9	0.5637	2.6982	0.5618	2.5776	0.5655	2.9505	0.4245	2.3667		
	270.000	4.3918–5.1912	9	0.2520	2.0155	0.3580	2.2676	0.2875	2.4933	0.2295	2.0634		
	280.000	5.9215–6.9677	9	0.5315	1.4138	0.2111	1.9494	0.3067	2.0572	0.1283	1.7661		
	290.000	7.8164–9.1488	9	0.9661	0.8584	0.2796	1.5946	0.4678	1.6473	0.2317	1.4413		
	300.000	10.1258–11.7937	9	1.3126	0.4712	0.4023	1.2860	0.6455	1.3103	0.4069	1.1613		
	310.000	12.8991–14.9716	9	1.5890	0.2514	0.6014	0.9823	0.8681	0.9941	0.6077	0.8878		
	320.000	16.1855–18.7318	9	1.7670	0.2250	0.8070	0.7136	1.0442	0.7397	0.7811	0.6473		
	330.000	20.0543–23.1335	9	1.8532	0.3378	0.9912	0.4752	1.1708	0.5426	0.9288	0.4373		
	340.000	24.5645–28.2556	9	1.8442	0.3953	1.1426	0.2969	1.2460	0.4020	1.0502	0.2896		
	230.000–340.000	0.997–28.256	108	1.3569	1.7900	0.6497	1.7734	0.8386	2.0561	0.5850	1.6589		
				Kij=0.0208		Kij=–0.0042		Kij=0.0073		Kij=0.0000		Kij=–0.0094	
Propane – Isopentane	273.160	0.5000–4.0000	8	5.2369	2.8838	4.0292	2.5424	1.8626	2.6297	2.6927	2.6297	6.6416	3.2748
	298.160	1.5000–7.0000	7	4.5397	2.4569	4.2594	2.9084	0.3382	2.6426	2.9533	2.9533	6.5673	3.5997
	348.160	5.0000–25.0000	8	2.5885	2.2491	3.3734	2.8757	1.8376	2.7171	2.7347	2.7347	4.3394	3.1316
	398.160	15.0000–35.0000	6	0.9689	3.4614	4.5019	3.8737	2.6247	3.7131	3.4363	3.4363	5.2650	3.8582
	273.160–398.160	0.500–35.000	29	3.7190	3.5061	4.6452	4.4455	2.6284	3.6998	3.7062	3.7062	6.0162	4.7788

Table 5.6 Comparison of percent AAD with and without Kij for systems containing nitrogen using five equations of state

SYSTEM	T (K)	Range of P (atm)	N	SRK EOS AAD(%) (with Kij)	SRK EOS AAD(%) (Kij=0)	PR EOS AAD(%) (with Kij)	PR EOS AAD(%) (Kij=0)	PT EOS AAD(%) (with Kij)	PT EOS AAD(%) (Kij=0)	MSRK EOS AAD(%) (with Kij)	MSRK EOS AAD(%) (Kij=0)	MPR EOS AAD(%) (with Kij)	MPR EOS AAD(%) (Kij=0)
Nitrogen – Methane				Kij=0.0306		Kij=0.0306		Kij=0.0694		Kij=0.0292		Kij=0.1181	
	113.716	8.24–57.48	8	1.0570	6.8971	1.3100	7.8727	9.0163	7.5608	1.1862	6.7796	19.5283	10.9554
	122.049	2.7559–25.8575	10	0.7585	5.1293	0.7147	5.5328	7.1438	5.5639	0.6598	4.9355	14.8913	8.3574
	127.604	3.4840–28.3752	7	0.9996	4.5888	0.9277	5.0496	8.1722	5.0003	1.0090	4.3968	15.8200	8.1208
	138.466	6.8216–33.8869	7	1.0283	4.5306	0.7061	5.1203	8.7261	5.0644	0.9727	4.3440	16.3050	8.6144
	149.827	12.1802–33.6828	7	0.7109	4.3012	0.4434	4.8803	6.8472	4.9166	0.6871	3.9642	15.5570	7.9508
	160.938	17.0115–40.6915	8	0.8329	3.1785	0.6631	3.5396	4.8364	3.6671	0.7251	2.7133	10.4394	5.6721
	172.049	25.2110–40.6915	7	1.0015	2.3329	0.8638	2.5257	1.8129	2.7378	0.5327	2.0633	3.9078	3.7293
	113.716–172.049	2.756–57.480	54	0.9053	4.4847	0.8059	4.9937	6.6883	4.9907	0.8204	4.2347	13.8478	7.6945
Nitrogen – Ethane				Kij=0.0417		Kij=0.0542		Kij=0.0479		Kij=0.0375		Kij=0.0771	
	138.716	3.4840–34.0230	7	5.9356	32.3685	6.3594	40.0546	5.0081	35.0510	9.5190	33.0252	4.7925	46.2242
	149.827	3.4023–40.8956	8	4.0853	27.7705	4.6523	35.3625	3.8982	30.3672	5.6610	27.4496	4.5001	42.9489
	172.049	3.5724–67.9099	8	4.0255	19.0922	4.5943	25.7238	4.2257	21.2451	4.2790	15.4013	4.7039	35.0984
	194.271	3.4703–96.2851	9	4.4420	13.2213	5.1413	17.9416	4.8227	14.6615	9.1401	5.8933	5.5538	27.0755
	260.000	18.1000–93.8000	8	1.3223	4.3929	1.2924	5.3043	1.2642	4.4210	11.6561	7.1863	2.3306	8.8144
	280.000	29.5000–80.9000	14	1.7345	3.7538	1.3920	4.3646	1.3357	3.6693	7.3690	5.0618	2.2209	5.6436
	138.716–280.000	3.402–96.285	54	3.354	14.9661	3.6035	19.1497	3.1901	16.2397	7.8672	13.9885	3.3315	24.8362
Nitrogen – Carbon dioxide				Kij=–0.0267		Kij=–0.0111		Kij=–0.0285		Kij=–0.0962		Kij=0.0479	
	220.000	14.8927–136.1559	8	3.0436	10.1717	3.8571	4.5135	3.1358	10.9830	8.6401	34.5175	4.7782	18.5488
	240.000	20.7254–142.8275	14	2.8089	8.8192	3.4345	5.1341	2.9137	10.0382	3.7171	34.5196	4.7757	11.1939
	270.000	39.0000–95.0000	18	1.5132	1.0261	1.4600	0.8837	1.3352	1.7124	4.6696	14.9220	2.3684	6.5873
	220.000–270.000	14.893–142.528	40	2.2728	5.5828	2.6305	3.0973	2.2478	6.4805	5.1303	25.6993	3.6929	10.5919

Table 5.7 Comparison of percent AAD with and without Kij for systems containing carbon dioxide using five equations of state

SYSTEM	T (K)	Range of P (atm)	N	SRK EOS AAD(%) (with Kij)	SRK EOS AAD(%) (Kij=0)	PR EOS AAD(%) (with Kij)	PR EOS AAD(%) (Kij=0)	PT EOS AAD(%) (with Kij)	PT EOS AAD(%) (Kij=0)	MSRK EOS AAD(%) (with Kij)	MSRK EOS AAD(%) (Kij=0)	MPR EOS AAD(%) (with Kij)	MPR EOS AAD(%) (Kij=0)
Carbon dioxide – Methane				Kij=0.0986		Kij=0.0986		Kij=0.0958		Kij=0.0889		Kij=0.1069	
	219.260	13.795–38.105	5	3.7706	34.1365	4.1666	35.9374	3.5396	33.9732	5.7296	33.1184	5.0144	37.6870
	230.000	15.000–69.080	13	1.2197	19.8285	1.7600	20.9582	1.3948	19.8375	1.8921	17.8644	3.1206	21.6092
	240.000	20.765–74.947	10	1.4638	19.3292	2.1103	20.3698	1.6517	19.8250	2.3877	16.9939	3.4589	21.1724
	250.000	20.000–77.000	8	1.7183	14.0834	2.3079	15.1899	2.1495	14.2621	2.5971	12.1190	2.5925	16.1699
	270.000	36.250–69.904	7	1.5396	10.7940	1.3985	11.6582	1.5149	11.1116	0.5906	9.2088	2.1965	12.5936
	219.260–270.000	13.795–77.000	43	1.7179	18.8365	2.1644	19.9760	1.8639	18.8949	2.3729	16.9577	3.1708	20.8975
Carbon dioxide – Ethane				Kij=0.1347		Kij=0.1319		Kij=0.1375		Kij=0.1403		Kij=0.1319	
	250.000	14.230–18.510	13	0.4264	17.0693	0.4237	17.6879	0.4218	17.9777	0.4893	17.8051	0.6448	17.7777
Carbon dioxide – Propane				Kij=0.1347		Kij=0.1292		Kij=0.1333		Kij=0.1361		Kij=0.1292	
	244.271	4.9674–13.4051	10	1.9912	30.8610	1.7420	30.8858	1.6395	31.5814	1.7801	31.1561	2.1650	30.6217
	266.493	7.9614–25.7894	11	2.0193	26.6549	1.9755	26.9072	1.9502	27.4974	1.9844	27.0257	2.0416	26.9228
	244.271–266.493	4.967–25.789	21	2.0059	28.6578	1.8643	28.8018	1.8022	29.4422	1.8871	28.9926	2.1004	28.6842
Carbon dioxide – n–Butane				Kij=0.1653		Kij=0.1500		Kij=0.1569		Kij=0.1611		Kij=0.1542	
	368.160	15.1098–70.0913	8	0.7126	14.5056	0.6260	14.4407	0.6170	14.8061	0.6789	14.6235	0.7147	14.8951
	393.160	23.6072–43.4148	5	0.7225	7.1529	0.4715	7.2307	0.4805	7.5513	0.5474	7.4612	0.4394	7.5750
	368.160–393.160	15.110–70.091	13	0.7164	11.6777	0.5666	11.6676	0.5645	12.0158	0.6284	11.8688	0.6088	12.0796
Carbon dioxide – i–Butane				Kij=0.1347		Kij=0.1250		Kij=0.1500		Kij=0.1347		Kij=0.1292	
	310.938	7.1448–55.1853	8	1.5774	21.1993	1.6902	21.0439	5.1186	21.6441	1.7843	21.4441	2.0654	21.6057
	344.271	21.3664–61.7858	6	2.1754	20.1577	1.6523	19.7401	1.4369	20.3560	1.8281	20.0204	1.8012	20.3386
	310.938–344.271	7.145–61.786	14	1.8320	20.7529	1.6740	20.4851	3.5407	21.0920	1.8031	20.8339	1.9522	21.0627

Table 5.7 (Continued)

SYSTEM	T (K)	Range of P (atm)	N	SRK EOS AAD(%) (with Kij)	SRK EOS AAD(%) (Kij=0)	PR EOS AAD(%) (with Kij)	PR EOS AAD(%) (Kij=0)	PT EOS AAD(%) (with Kij)	PT EOS AAD(%) (Kij=0)	MSRK EOS AAD(%) (with Kij)	MSRK EOS AAD(%) (Kij=0)	MPR EOS AAD(%) (with Kij)	MPR EOS AAD(%) (Kij=0)
Carbon dioxide – n–Pentane				Kij=0.1403		Kij=0.1319		Kij=0.1319		Kij=0.1389		Kij=0.1319	
	277.660	2.2455–7.0170	10	5.5156	26.1161	5.0976	26.0731	5.0153	26.0731	5.2405	26.3088	5.1661	25.9906
	311.049	4.5591–61.5136	10	5.0503	28.9827	5.1385	28.7151	5.0462	28.7151	4.8972	28.8669	5.0612	28.7274
	344.160	4.0828–88.4548	14	2.4229	24.0683	2.9190	23.6726	2.9219	23.6726	2.7794	23.5580	2.8001	23.6864
	377.604	8.9621–87.5072	8	3.6066	22.0162	2.5798	21.5043	2.7117	21.5043	2.6743	21.0954	2.6805	21.5321
	408.160	13.8169–71.9270	7	3.7512	15.3595	2.9512	14.9651	3.0603	14.9651	3.1861	14.4780	2.9465	14.9674
	438.160	21.7715–58.3173	5	4.0437	10.0426	3.2876	9.7680	3.2298	9.7680	2.9349	9.2313	3.3168	9.7694
	277.660–438.160	2.246–88.455	54	3.9798	22.6260	3.7215	22.3135	3.7183	22.3135	3.6789	22.1821	3.7061	22.3086
Carbon dioxide – i–Pentane				Kij=0.1694		Kij=0.1500		Kij=0.1528		Kij=0.1542		Kij=0.1528	
	408.160	15.919–71.720	9	1.2176	13.8954	1.2907	13.4346	1.4259	13.6141	1.7084	12.9750	1.3493	13.6647
Carbon dioxide – n–Heptane				Kij=0.1125		Kij=0.1000		Kij=0.0917		Kij=0.1069			
	310.660	8.7099–52.9398	10	2.9876	34.1624	3.8889	33.4457	4.0257	31.5215	4.2534	34.1349		
	352.604	4.1848–114.5895	14	0.8007	22.5751	0.8781	21.7021	0.8510	20.0684	0.8718	21.5673		
	394.271	11.1595–130.6483	15	3.0943	17.9437	3.8369	16.6735	4.4070	14.6735	4.5524	15.5579		
	477.216	17.2837–95.8088	6	1.5076	10.1635	2.0890	9.5278	2.4016	9.9479	2.9540	6.1698		
	310.660–477.216	4.185–130.648	45	2.1455	21.9514	2.6949	21.0123	2.9486	19.4658	3.1278	20.3039		
Carbon dioxide – n–Decane				Kij=0.1500		Kij=0.1167		Kij=0.0722		Kij=0.1056			
	462.560	19.3600–50.7000	4	2.2030	20.8657	1.5624	18.1558	0.9847	11.6498	0.6666	15.6394		
	476.960	14.2500–50.1000	4	1.3708	19.1248	1.3290	16.3488	1.2331	10.1197	0.9245	13.3732		
	542.960	29.3800–51.0000	4	4.1498	14.7242	2.7818	12.2072	2.1249	7.8528	1.0050	7.8024		
	583.660	19.7600–50.4000	4	7.3639	12.5779	6.3181	11.0052	5.6265	8.5924	3.9667	7.2481		
	462.560–583.660	14.250–51.000	16	3.7719	16.8231	2.9978	14.4292	2.4923	9.5537	1.6407	11.0158		

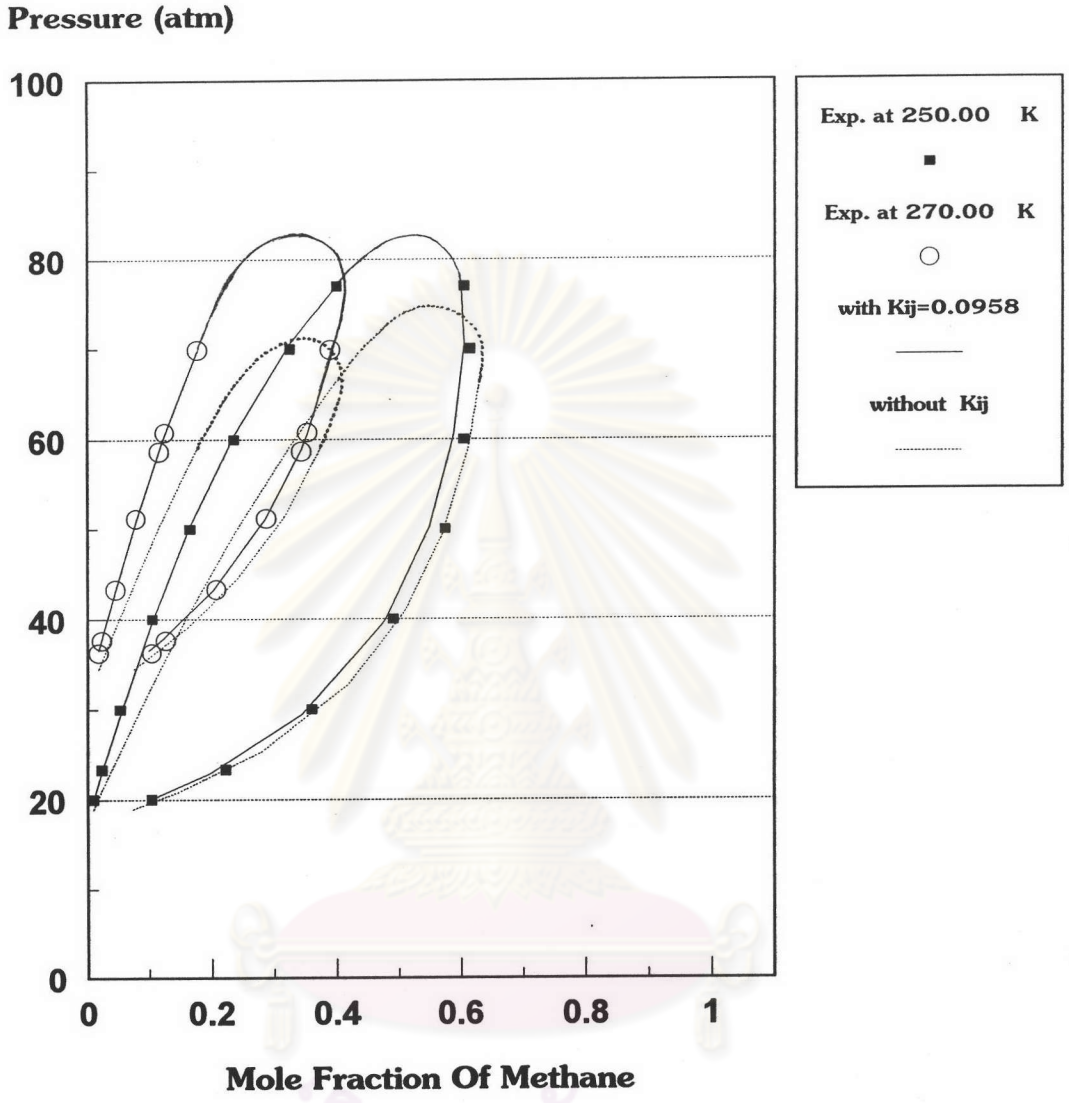


Figure 5.8 (a) Comparison of the VLE results calculated with and without Kij (of PT equation) for CO2 - Methane system at 250.00 K and 270.00 K

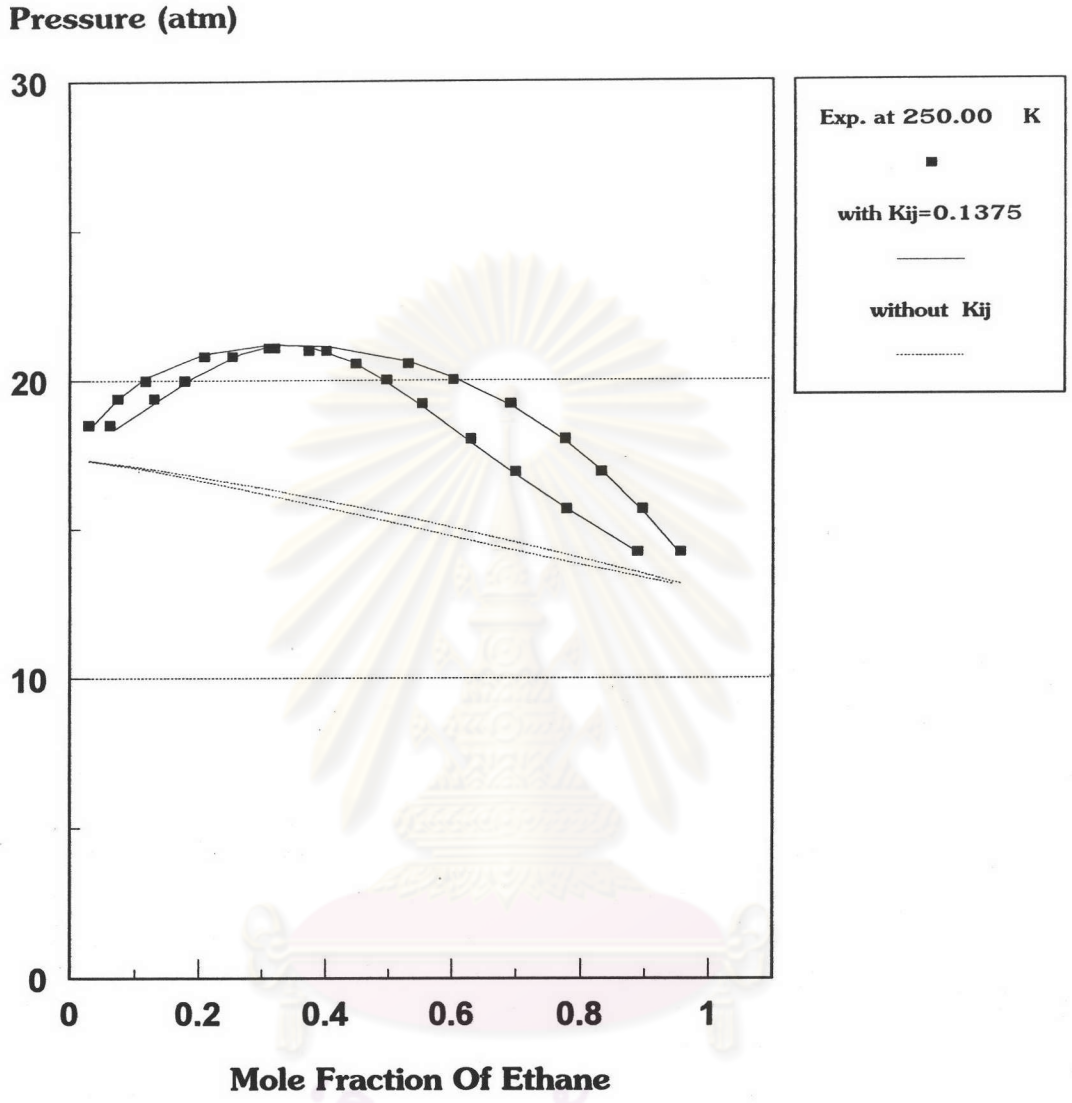


Figure 5.8 (b) Comparison of the VLE results calculated with and without Kij (of PT equation) for CO2 - Ethane system at 250.00 K

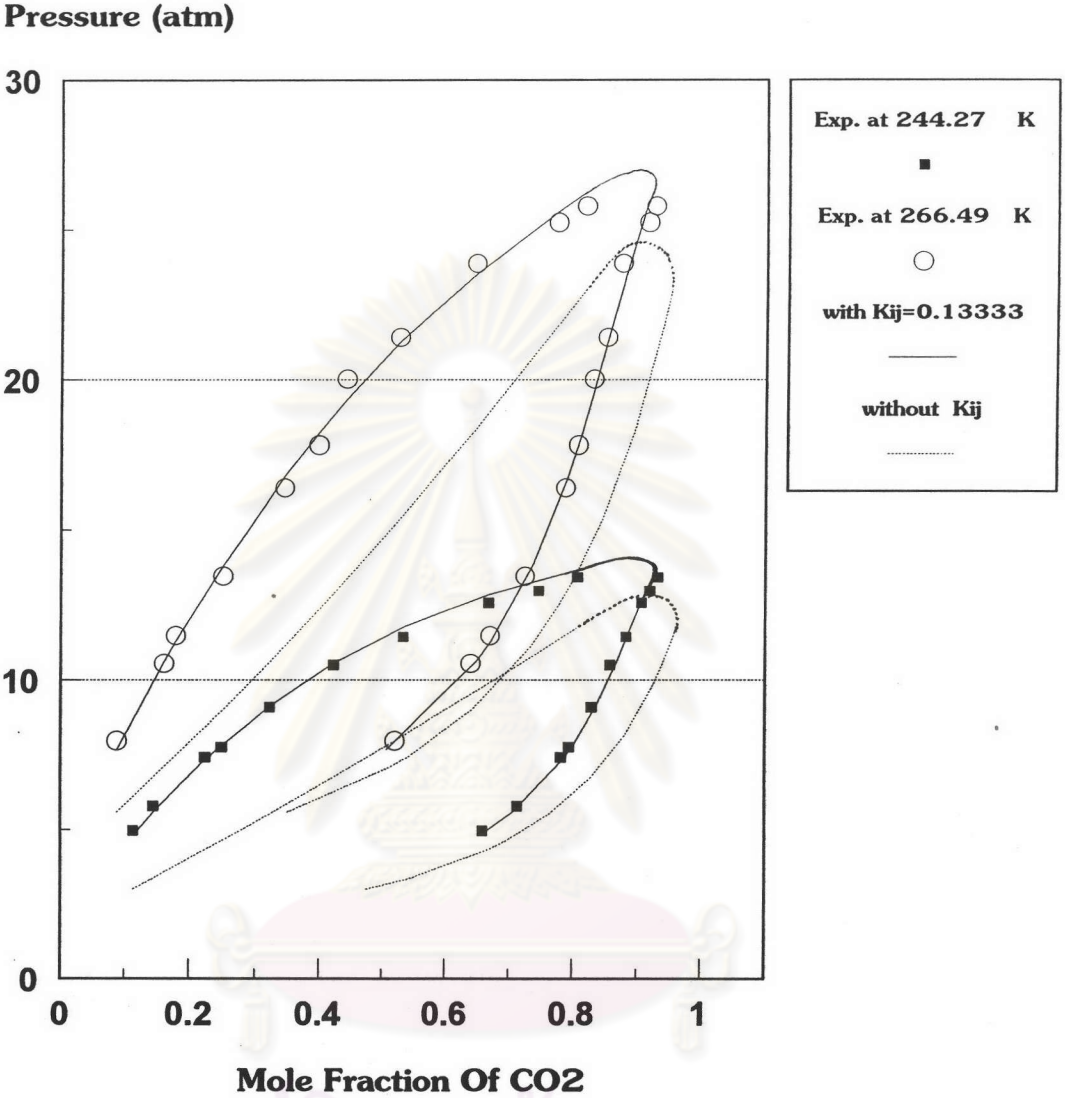


Figure 5.8 (c) Comparison of the VLE results calculated with and without Kij (of PT equation) for CO2 – Propane system at 244.27 K and 266.49 K

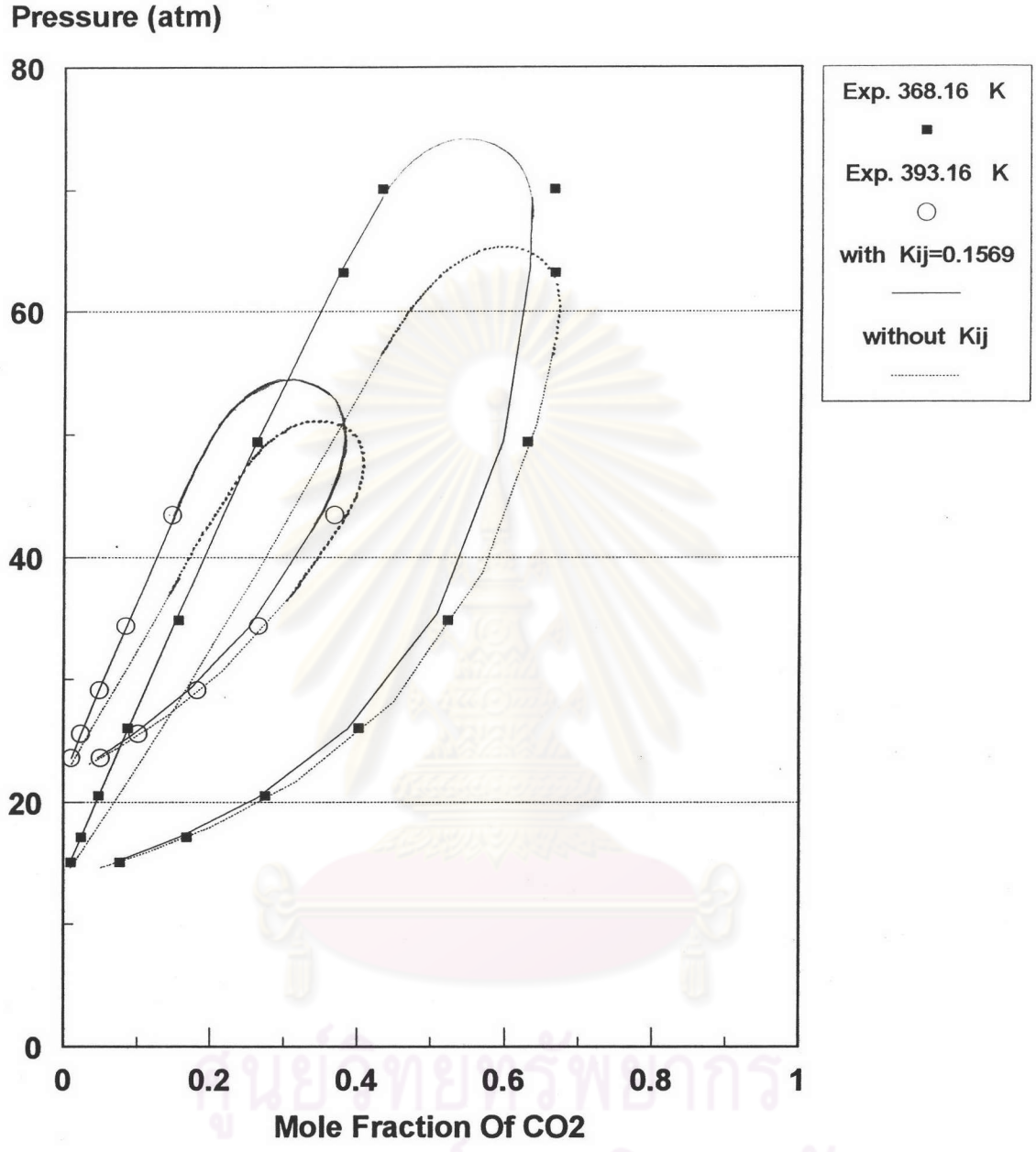


Figure 5.8 (d) Comparison of the VLE results calculated with and without Kij (of PT equation) for CO2 - n-Butane system at 368.16 K and 393.16 K

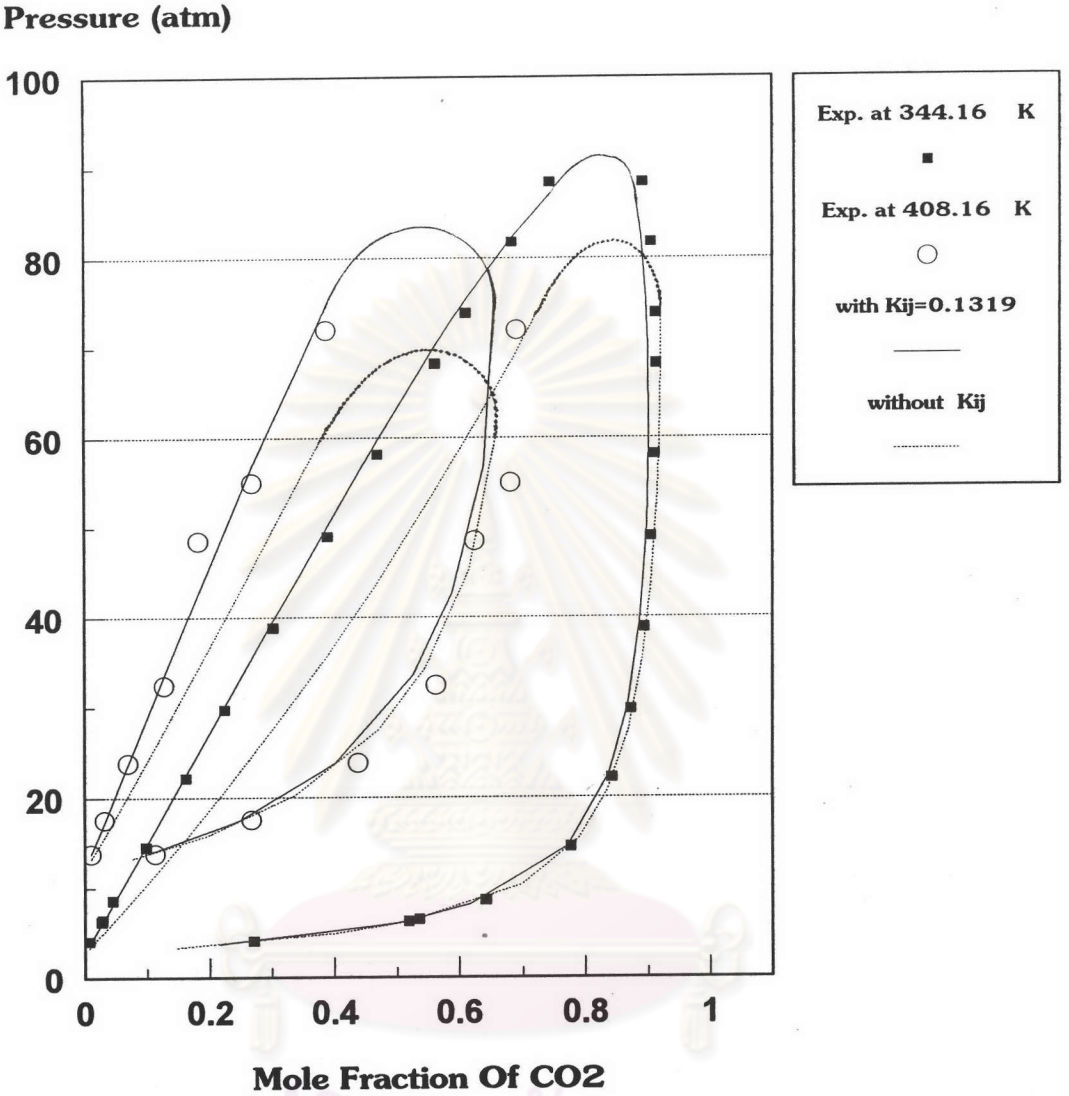


Figure 5.8 (e) Comparison of the VLE results calculated with and without Kij (of PT equation) for CO2 - n-Pentane system at 3244.16 K and 408.16 K

5.3 Temperature Dependence of Binary Interaction Parameters

As shown in Figures 5.9 to 5.13, the K_{ij} values obtained from the SRK equation using bubble point pressure criterion for methane, ethane, propane, nitrogen and carbon dioxide do vary to some degree with temperature. Only systems containing CO_2 depend on temperatures, especially for CO_2 - n-pentane and CO_2 - n-decane. The relationship between K_{ij} value and temperature for these systems is the polynomial function as shown in Figure 5.13.

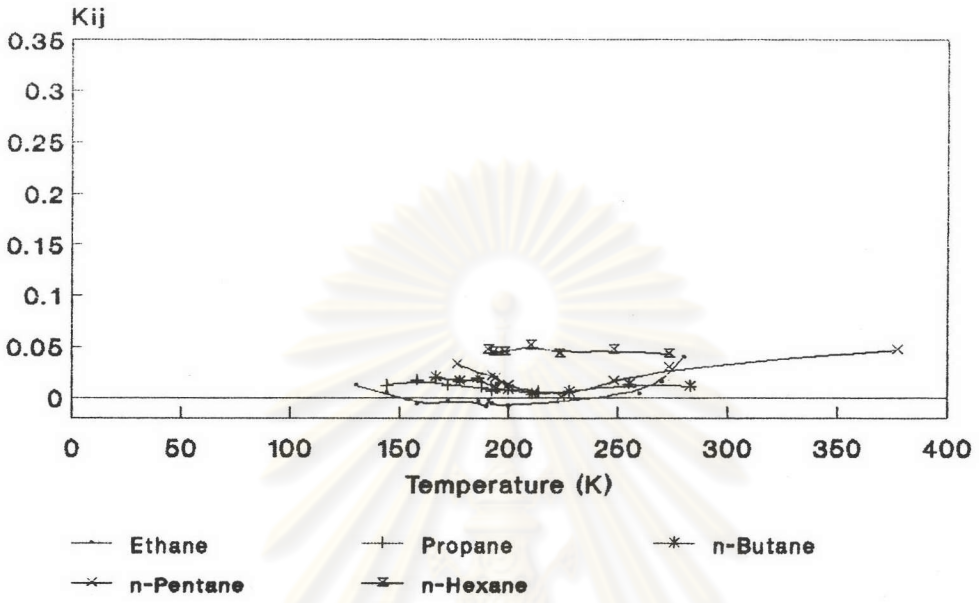


Figure 5.9 KIj value as a function of temperature for systems containing methane

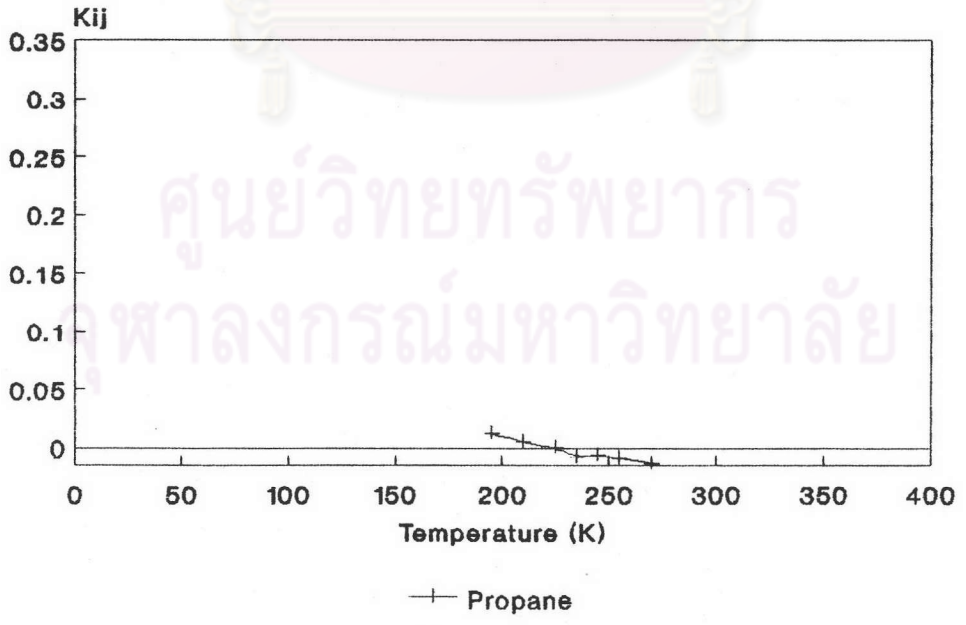


Figure 5.10 KIj value as a function of temperature for systems containing ethane

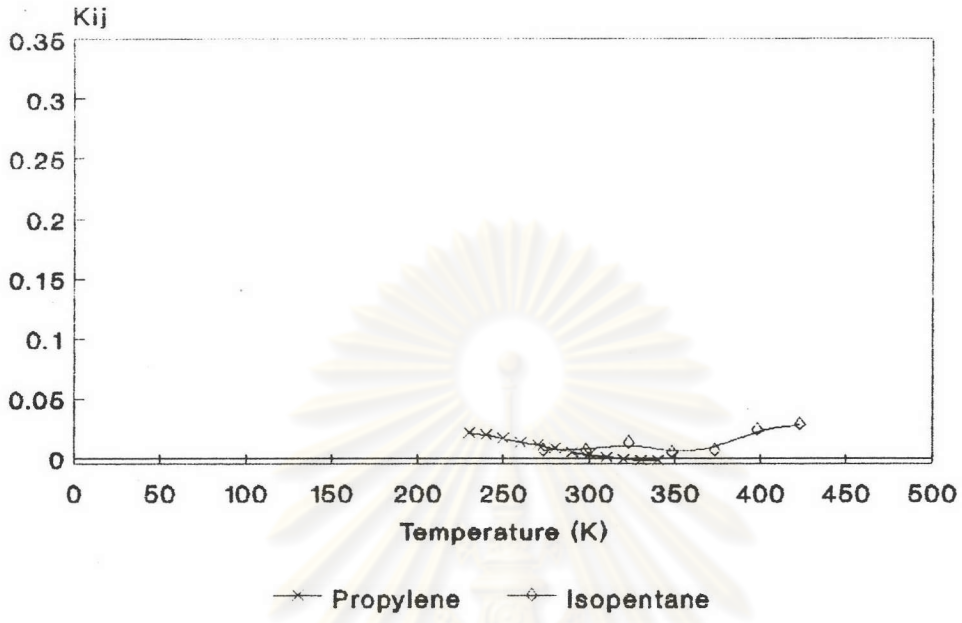


Figure 5.11 KIj value as a function of temperature for systems containing propane

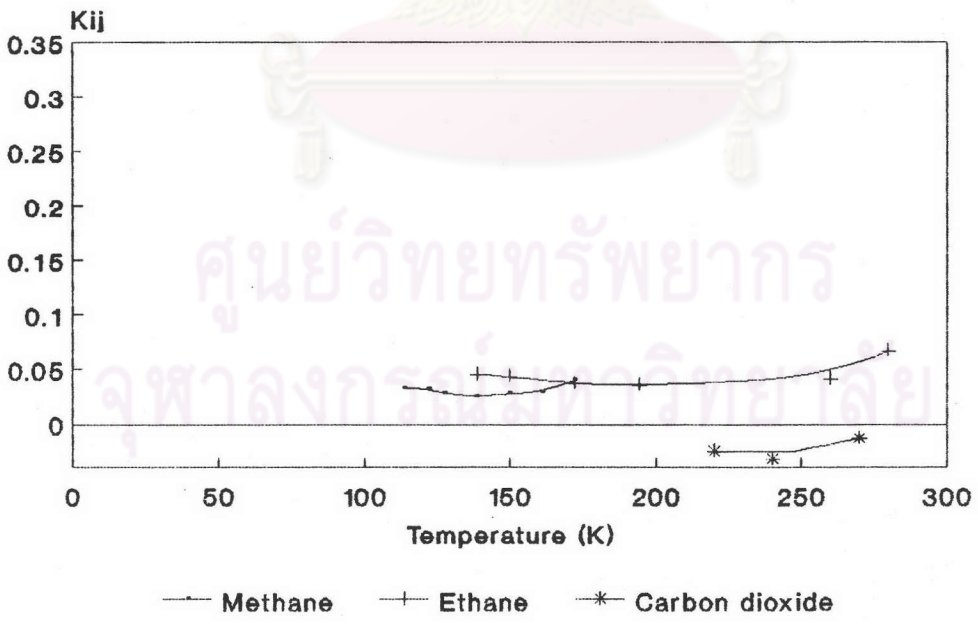


Figure 5.12 KIj value as a function of temperature for systems containing nitrogen

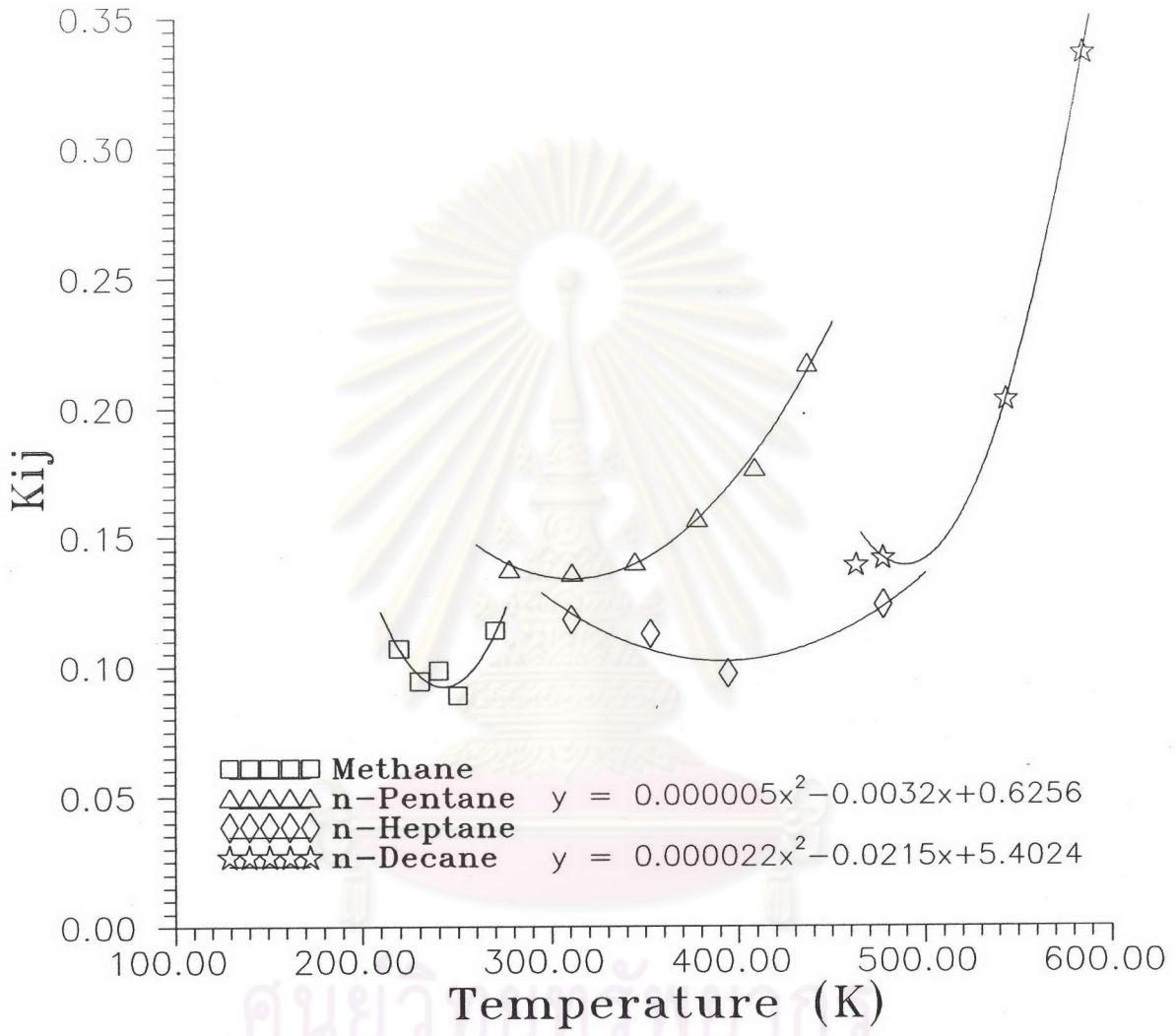


Figure 5.13 Kij value as a temperature for systems containing CO2

5.4 Comparison of the Optimum Binary Interaction Parameters of Some Equations of State with Earlier Works

Graboski and Daubert [25] have reported an extensive tabulation of the binary interaction parameters for mixtures containing non-hydrocarbon components with hydrocarbons using the SRK equation. The minimization of the bubble point pressure deviations was employed. Reevaluation of this procedure in search of the optimum K_{ij} for VLE calculations with the SRK equation was presented by Eillott and Daubert [56] in 1985. The same objective function was used but a larger data base was employed, this resulted in slight improvements for the previous one.

Nishiumi et al. [57] proposed a K_{ij} correlation in terms of the ratio of critical molar volumes and in addition absolute difference between the acentric factors of each component using the PR equation.

The K_{ij} values found in this work and those proposed by Graboski and Daubert [25], Eillot and Daubert [56], and Nishiumi et al. [57] for systems containing methane, ethane, propane, nitrogen and carbon dioxide are shown in Table 5.6. The comparison indicates that there is agreement between these works. The small deviations of results may be due to the different data base employed and the different algorithms used in the calculation methods.

Table 5.8 Kij values in this work and of the SRK equation as predicted by Graboski and Daubert [25], Eillott and Daubert [56] and of the PR equation as predicted by Nishiumi et al. [57]

System	Kij				
	SRK EOS			PR EOS	
	this work	[25]	[56]	this work	[57]
Methane – Ethane	−0.0028	–	–	−0.0028	0.056
Methane – Propane	0.0094	–	–	0.0177	0.015
Methane – n–Butane	0.0115	–	–	0.0188	0.025
Methane – Isobutane	0.0319	–	–	0.0306	0.031
Methane – n–Pentane	0.0181	–	–	0.0264	0.031
Methane – Isopentane	0.0292	–	–	0.0319	0.035
Methane – Neopentane	0.0417	–	–	0.0417	0.040
Methane – n–Hexane	0.0458	–	–	0.0521	0.038
Ethane – Propane	0.0000	–	–	−0.0021	0.005
Ethane – n–Butane	0.0326	–	–	0.0306	0.011
Ethane – Isobutane	−0.0156	–	–	−0.0115	0.016
Propane – Propylene	0.0115	–	–	0.0104	−0.002
Propane – Isopentane	0.0208	–	–	−0.0042	–
Nitrogen – Methane	0.0306	0.0319	0.0350	0.0306	0.044
Nitrogen – Ethane	0.0417	0.0388	0.0375	0.0542	0.058
Nitrogen – Carbon dioxide	−0.0267	−0.0220	−0.0220	−0.0111	−0.016
Carbon dioxide – Methane	0.0986	0.0976	0.0936	0.0986	0.114
Carbon dioxide – Ethane	0.1347	0.1346	0.1340	0.1319	0.113
Carbon dioxide – Propane	0.1347	0.1018	0.1280	0.1292	0.111
Carbon dioxide – n–Butane	0.1653	0.1474	0.1376	0.1500	0.110
Carbon dioxide – i–Butane	0.1347	0.1358	–	0.1250	0.110
Carbon dioxide – n–Pentane	0.1403	0.1278	0.1407	0.1319	0.109
Carbon dioxide – i–Pentane	0.1694	0.0262	0.1341	0.1500	0.109
Carbon dioxide – n–Heptane	0.1125	0.1136	0.1120	0.1000	–
Carbon dioxide – n–Decane	0.1500	0.1377	–	0.1167	0.101