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APPENDIX A

Group Contribution for Properties Estimation

Group Contribution for Properties Estimation

Table A.1 Volume increments (υ_i) for common elements and ions (Lyman et al., 1982).

Element or Ion	υ_i (Å^3)
-H	6.9
=C=	15.3
-C≡	15.3
>C=	13.7
>C<	11
=O	14
-O-	9.2
N≡	16
-N=	12.8
-N<	7.2
S	23.8
-F	12.8
-Cl	26.7
-Br	33
-I	45
Cl^-	28.9
Br^-	39.3
I^-	56.6
Na+	13.6
K+	27.3
H_2O	21.5
Benzene frame (carbons only)	75.2
O-H…O hydrogen-bond	-2.6
N-H…O hydrogen-bond	-2.8
N-H…N hydrogen-bond	-0.3
Non-aromatic rings (rough estimate)	-3
Naphthalene frame (carbons only)	123.7

Table A.2 First-order groups and their contributions for the physical properties (Gani method) (Constantinou and Gani, 1994).

Group	t_{c1i}	p_{c1i} (bar$^{-0.5}$)	v_{c1i} (m^3/kmol)	t_{b1i}
CH_3	1.6781	0.00199	0.07504	0.8894
CH_2	3.492	0.010558	0.05576	0.9225
CH	4.033	0.001315	0.03153	0.6033
C	4.8823	-0.0104	-0.00034	0.2878
$CH_2 = CH$	5.0146	0.025014	0.11648	1.7827
CH = CH	7.3691	0.017865	0.09541	1.8433
$CH_2=C$	6.5081	0.022319	0.09183	1.7117
CH=C	8.9582	0.01259	0.07 3 27	1.7957
C = C	11.3764	0.002044	0.07618	1.8881
$CH_2 = C = CH$	9.9318	0.03127	0.14831	3.1243
ACH	3.7337	0.007542	0.04215	0.9297
AC	14.6409	0.002136	0.03985	1.6254
$ACCH_3$	8.213	0.01936	0.10364	1.9669
$ACCH_2$	10.3239	0.0122	0.10099	1.9478
ACCH	10.4664	0.002769	0.0712	1.7444
OH	9.7292	0.005148	0.03897	3.2152
ACOH	25.9145	-0.00744	0.03162	4.4014
CH_3CO	13.2896	0.025073	0.13396	3.5668
CH_2CO	14.6273	0.017841	0.11195	3.8967
CHO	10.1986	0.014091	0.08635	2.8526
CH_3COO	12.5965	0.02902	0.1589	3.636
CH_2COO	3.8116	0.021836	0.13649	3.3953
HCOO	11.6057	0.013797	0.10565	3.1459
CH_3O	6.4737	0.02044	0.08746	2.2536
CH_2O	6.0723	0.015135	0.07286	1.6249
CH-O	5.0663	0.009857	0.05865	1.1557
FCH_2O	9.5059	0.009011	0.06858	2.5892
CH_2NH_2	12.1726	0.012558	0.13128	3.1656
$CHNH_2$	10.2075	0.010694	0.07527	2.5983
CH_3NH	9.8544	0.0 12589	0.12152	3.1376
CH_2NH	10.4677	0.01039	0.09956	2.6127
CHNH	7.2121	-0.00046	0.09165	1.578
CH_3N	7.6924	0.015874	0.12598	2.1647
CH_2N	5.5172	0.004917	0.06705	1.2171
$ACNH_2$	28.757	0.00112	0.06358	5.4736
C_5H_4N	29.1528	0.029565	0.24831	6.28
C_5H_3N	27.9464	0.025653	0.17027	5.9234
CH_2CN	20.3781	0.036133	0.15831	5.0525
COOH	23.7593	0.011507	0.10188	5.8337
CH_2CL	11.0752	0.019789	0.11564	2.9637
CHCL	10.8632	0.01136	0.1035	2.6948
CCL	11.3959	0.003086	0.07922	2.2073
$CHCL_2$	16.3945	0.026808	0.16951	3.93
CCL_2	****	****	****	3.56
CCL_3	18.5875	0.034935	0.21031	4.5797
ACCL	14.1565	0.013135	0.10158	2.6293
$ACNO_2$	34.587	0.01505	0.14258	6.0837

Table A.2 First-order groups and their contributions for the physical properties (Gani method) (Constantinou and Gani, 1994) (Cont').

Group	t_{c1i}	p_{c1i} (bar$^{-0.5}$)	v_{c1i} (m^3/kmol)	t_{b1i}
CH_2SH	13.8058	0.013572	0.10252	3.2914
I	17.3947	0.002753	0.10814	3.665
BR	10.5371	-0.00177	0.08281	2.6495
CH ≡ C	7.5433	0.014827	0.09331	2.3678
C≡C	11.4501	0.004115	0.07627	2.5645
CL-(C=C)	5.4334	0.016004	0.05687	1.7824
ACF	2.8977	0.013027	0.05672	0.9442
$HCON(CH_2)_2$	* * * *	****	* * * *	7.2644
CF_3	2.4778	0.044232	0.1148	1.288
CF_2	1.7399	0.012884	0.09519	0.6115
CF	3.5192	0.004673	****	1.1739
COO	12.1084	0.011294	0.08588	2.6446
CCL_2F	9.8408	0.035446	0.18212	2.8881
HCCLF	****	****	****	2.3086
$CCLF_2$	4.8923	0.039004	0.14753	1.9163
F (except as above)*	1.5974	0.014434	0.03783	1.0081
$CONH_2$	65.1053	0.004266	1.4431	10.3428
$CONCHCH_3$	****	****	****	****
$CONCHCH_2$	****	****	****	****
$CON(CH_3)_2$	36.1403	0.040149	2.5031	7.6904
$CONCH_3CH_2$	****	****	****	****
$CON(CH_2)_2$	****	****	****	6.7822
$C_2H_5O_2$	17.9668	0.025435	0.16754	5.5566
$C_2H_4O_2$	****	****	****	5.4248
CH_3S	14.3969	0.016048	0.13021	3.6796
GH_2S	17.7916	0.011105	0.1165	3.6763
CHS	****	****	****	2.6812
C_4H_3S	****	****	****	5.7093
C_4H_2S	****	****	****	5.826
CH2NO2	24.7369	0.020974	0.16531	5.7619
CHNO2	23.205	0.012241	0.14227	5.0767

Table A.3 Second-order groups and their contributions for the physical properties (Gani method) (Constantinou and Gani, 1994).

Group	t_{c2i}	p_{c2i} (bar$^{-0.5}$)	v_{c2i} (m^3/kmol)	t_{b2i}
$(CH_3)_2CH$	-0.5334	0.000488	0.004	-0.1157
$(CH_3)_3C$	-0.5143	0.00141	0.00572	-0.0489
$CH(CH_3)CH(CH_3)$	1.0699	-0.001849	-0.00398	0.1798
$CH(CH_3)C(CH_3)_2$	1.9886	-0.005198	-0.01081	0.3189
$CH(CH_3)_2C(CH_3)_2$	5.8254	-0.01323	-0.023	0.7273
3 membered ring*	-2.3305	0.003714	-0.00014	0.4745
4 membered ring*	-1.2978	0.001171	-0.00851	0.3563
5 membered ring*	-0.6785	0.000424	-0.00866	0.1919
6 membered ring'	0.8479	0.002257	0.01636	0.1957
7 membered ring'	3.6714	-0.009799	-0.027	0.3489
$CH_n=CH_m-CH_p=CH_k$;k,n,m,p € (0,2)	0.4402	0.004186	-0.00781	0.1589
$CH_3=CH_m=CH_n$;m,n € (0,2)	0.0167	-0.000183	-0.00098	0.0668
$CH_2=CH_m=CH_n$;m,n € (0,2)	-0.5231	0.003538	0.00281	-0.1406
$CH-CH_m=CH_n$ or $C-CH_m=CH_n$;m,n € (0,2)	-0.385	0.005675	0.00826	-0.09
Alicyclic side chain $C_{cyclic}C_m$;m>1	2.116	-0.002546	-0.01755	0.0511
$CH_3=CH_3$	2.0427	0.005175	0.00227	0.6884
CHCHO or CCHO	-1.5826	0.003659	-0.00664	-0.1074
CH_3COCH_2	0.2996	0.001474	-0.0051	0.0224
CH_3COCH or CH_3COC	0.5018	-0.002303	-0.00122	0.092
C_{cyclic} (=O)	2.9571	0.003818	-0.01966	0.558
ACCHO	1.1696	-0.002481	0.00664	0.0735
CHCHOOH or CCOOH	-1.7493	0.00492	0.00559	-0.1552
ACCOOH	6.1279	0.000344	-0.00415	0.7801
CH_3COOCH or CH_3COOC	-1.3406	0.000659	-0.00293	-0.2383
$COCH_2COO$ or COCHCOO or COCCOO	2.5413	0.001067	-0.00591	0.4456
CO-O-CO	-2.7617	-0.004877	-0.00144	-0.1977
ACCOO	-3.4235	-0.000541	0.02605	0.0835
CHOH	-2.8035	-0.004393	-0.00777	-0.5385
COH	-3.5442	0.000178	0.01511	-0.6331
$CH_m(OH)CH_n(OH)$;m,n € (0,2)	5.4941	0.005052	0.00397	1.4108
$CH_{m\ cyclic}$-OH m € (0,1)	0.3233	0.006917	-0.00297	-0.069
$CH_m(OH)CH_n(NH_p)$ m,n,p € (0,3)	5.4864	0.001408	0.00433	1.0682
$CH_m(NH_2)CH_n(NH_2)$;m,n € (0,2)	2.0699	0.002148	0.0058	0.4247
$CH_{m\ cyclic}$-NHp-$CH_{n\ cyclic}$;m,n,p € (0,2)	2.1345	-0.005947	-0.0138	0.2499
$CH_m-O-CH_n=CH_p$ m,n,p € (0,2)	1.0159	-0.000878	0.00297	0.1134
AC-O-CH_m;m € (0,3)	-5.3307	-0.002249	-0.00045	-0.2596
$CH_{m\ cyclic}$-S-$CH_{n\ cyclic}$ m,n € (0,2)	4.4847	* * * *	* * * *	0.4408
$CH_m=CH_n$-F;m,n € (0,2)	--0.4996	0.000319	-0.00596	-0.1168
$CH_m=CH_n$-Br;m,n € (0,2)	-1.9334	-0.004305	0.00507	-0.3201
$CH_m=CH_n$-I;m,n € (0,2)	****	****	* * * *	-0.4453
ACBr	-2.2974	-0.009027	-0.00832	-0.6776
ACI	2.8907	0.008247	-0.00341	-0.3678
CHm(NH2)-COOH;m € (0,2)	****	****	****	****

Table A.4 Groups and their contributions for the boiling point properties (Joback method) (Reid et al., 1987).

Group	Δ_{BJ}	Group	Δ_{BJ}
-CH3 (non-ring)	23.58	-OH (phenols)	76.34
>CH2 (non-ring)	22.88	-O- (non-ring)	22.42
>CH- (non-ring)	21.74	-O- (ring)	31.22
>C< (non-ring)	18.25	>C=O (non-ring)	76.75
=CH2 (non-ring)	18.18	>C=O (ring)	94.97
=CH- (non-ring)	24.96	-HC=O (aldehyde)	72.24
>C= (non-ring)	24.14	-COOH (acid)	169.09
=C= (non-ring)	26.15	-COO- (ester)	81.1
υCH (non-ring)	9.2	=O (any other)	-10.5
υC- (non-ring)	27.38	-NH2	73.23
>CH2 (ring)	27.15	>NH (non-ring)	50.17
>CH- (ring)	21.78	>NH (ring)	52.82
>C< (ring)	21.32	>N- (non-ring)	11.74
=CH- (ring)	26.73	-N=, HN= (non-ring)	74.6
>C= (ring)	31.01	-N= (ring)	57.55
-F	-0.03	-CN	125.66
-Cl	38.13	-NO2	152.54
-Br	66.86	-SH	63.56
-I	93.84	-S- (non-ring)	68.78
-OH (alcohol)	92.88	-S- (ring)	52.1

Table A.5 Groups and their contributions for the critical point properties (Joback method) (Reid et al., 1987).

Group	*tck*	*pck*	*vck*	n_A	Group	*tck*	*pck*	*vck*	n_A
-CH3 (non-ring)	0.0141	-0.0012	65	4	-OH (phenols)	0.024	0.0184	-25	2
>CH2 (non-ring)	0.0189	0	56	3	-O- (non-ring)	0.0168	0.0015	18	1
>CH- (non-ring)	0.0164	0.002	41	2	-O- (ring)	0.0098	0.0048	13	1
>C< (non-ring)	0.0067	0.0043	27	1	>C=O (non-ring)	0.038	0.0031	62	2
=CH2 (non-ring)	0.0113	-0.0028	56	3	>C=O (ring)	0.0284	0.0028	55	2
=CH- (non-ring)	0.0129	-0.0006	46	2	-HC=O (aldehyde)	0.0379	0.003	82	3
>C= (non-ring)	0.0117	0.0011	38	1	-COOH (acid)	0.0791	0.0077	89	4
=C= (non-ring)	0.0026	0.0028	36	1	-COO- (ester)	0.0481	0.0005	82	3
υCH (non-ring)	0.0027	-0.0008	46	2	=O (any other)	0.0143	0.0101	36	1
υC- (non-ring)	0.002	0.0016	37	1	-NH2	0.0243	0.0109	38	3
>CH2 (ring)	0.01	0.0025	48	3	>NH (non-ring)	0.0295	0.0077	35	2
>CH- (ring)	0.0122	0.0004	38	2	>NH (ring)	0.013	0.0114	29	2
>C< (ring)	0.0042	0.0061	27	1	>N- (non-ring)	0.0169	0.0074	9	1
=CH- (ring)	0.0082	0.0011	41	2	-N=, HN= (non-ring)	0.0225	-0.01	0	1
>C= (ring)	0.0143	0.0008	32	1	-N= (ring)	0.0085	0.0076	34	1
-F	0.0111	-0.0057	27	1	-CN	0.0496	0.0101	91	2
-Cl	0.0105	-0.0049	58	1	-NO2	0.0437	0.0064	91	3
-Br	0.0133	0.0057	71	1	-SH	0.0031	0.0084	63	2
-I	0.0068	-0.0034	97	1	-S- (non-ring)	0.0119	0.0049	54	1
-OH (alcohol)	0.0741	0.0112	28	2	-S- (ring)	0.0019	0.0051	38	1

Table A.6 K_F Factors for alicyclic[a] organic compounds (Constantinou and Gani, 1994).

Compound Type	Number of carbon atoms (N) in compound, including carbon atoms of functional group											
	1	2	3	4	5	6	7	8	9	10	11	12-20
Hydrocarbon												
n-Alkanes	0.97	1	1	1	1	1	1	1	1	1	1	1
Alkane isomers				0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99
Mono- and dipolefins and isomers		1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1
Cyclic saturated hydrocarbons			1	1	1	1	1	1	1	1	1	1
Alkyl derivatives of cyclic saturated hydrocarbons				0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99
Halides (saturated or unsaturated)												
Monochlorides	1.05	1.04	1.03	1.03	1.03	1.03	1.03	1.03	1.02	1.02	1.02	1.01
Monobromides	1.04	1.03	1.03	1.03	1.03	1.03	1.02	1.02	1.02	1.01	1.01	1.01
Monoiodides	1.03	1.02	1.02	1.02	1.02	1.02	1.01	1.01	1.01	1.01	1.01	1.01
Polyhalides (not entirely halogenated)	1.05	1.05	1.05	1.04	1.04	1.04	1.03	1.03	1.03	1.02	1.02	1.02
Mixed halides (completely halogenated)	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01
Perfluorocarbons	1	1	1	1	1	1	1	1	1	1	1	1
Compounds Containing the Ketone Group												
Esters		1.14	1.09	1.08	1.07	1.06	1.05	1.04	1.04	1.03	1.02	1.01
Ketones			1.08	1.07	1.06	1.06	1.05	1.04	1.04	1.03	1.02	1.01
Aldehydes	-	1.09	1.08	1.08	1.07	1.06	1.05	1.04	1.04	1.03	1.02	1.01
Nitrogen Compounds												
Primary amines	1.16	1.13	1.12	1.11	1.1	1.1	1.09	1.09	1.08	1.07	1.06	1.05b
Secondary amines		1.09	1.08	1.08	1.07	1.07	1.06	1.05	1.05	1.04	1.04	1.03b
Tertiary amines			1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01
Nitriles	-	1.05	1.07	1.06	1.06	1.05	1.05	1.04	1.04	1.03	1.02	1.01
Nitro compounds	1.07	1.07	1.07	1.06	1.06	1.05	1.05	1.04	1.04	1.03	1.02	1.01
Sulfur compounds												
Mercaptans	1.05	1.03	1.02	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01
Sulfides		1.03	1.02	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01
Alcohols												
Alcohols (single-OH group)	1.22	1.31	1.31	1.31	1.31	1.3	1.29	1.28	1.27	1.26	1.24	1.24b
Diols (glycols or condensed glycols)		1.33	1.33	1.33	1.33	1.33	1.33	1.33				
Triols (glycerol, etc.)			1.38	1.38	1.38							
Cyclohexanol, cyclohexyl methyl alcohol, etc.						1.2	1.2	1.21	1.24	1.26		
Miscellaneous Compounds												
Ethers (aliphatic only)		1.03	1.03	1.02	1.02	1.02	1.01	1.01	1.01	1.01	1.01	1.01
Oxides (cyclic ethers)		1.08	1.07	1.06	1.05	1.05	1.04	1.03	1.02	1.01	1.01	1.01

Carbocyclic or heterocyclic compounds having aliphatic properties.
For $N = 12$ only; no prediction is made for K_F where $N > 12$

Notes:

1. Consider any phenyl group as a single carbon atom.
2. K_F factors are the same for all aliphatic isomers of a given compound. For example, $K_F = 1.31$ for n-butyl alcohol, i-butyl alcohol, t-butyl alcohol, and s-butyl alcohol.
3. In organometallic compounds, consider any methallic atom as a carbon atom.
4. For compounds not included in this table, assume $K_F = 1.06$.

Table A.7 Values of K_F for aromatic hydrogen bonded system (Constantinou and Gani, 1994).

Compound Type	K_F
Phenols (single-OH)	1.15
Phenols (more than one-OH)	1.23
Anilines (single-NH_2)	1.09
Anilines (more than one - NH_2)	1.14
N-substituted anilines (C_6H_5NHR)	1.06
Naphthols (single-OH)	1.09
Naphthylamines (single-NH_2)	1.06
N-substituted naphthylamines	1.03

Note: For mixed systems, K_F for OH group takes precedence. Thus, K_F for p-aminophenol is 1.15.

APPENDIX B

Source Codes

B.1 MATLAB commands for obtaining the Solubility of Solute in Supercritical Fluids

```
clear
% File name is solubility.m
% Plot solubility curve of solid solutes in supercritical fluids (SF)
% Solid solutes: Isoflavones (component 2)
% SF: Carbon dioxide (component 1)
% Cosolvent: Methanol and Water (component 3)

no = 2;

% Operating temperature
T = 343;                              % K
% Solute's critical temperature and pressure and acentric factor
vs   = 0.000399;                      % m^3/mol
 Tb  = 1173.33;                       % K

    Tc = zeros(no,1);
    Pc = zeros(no,1);
    Vc = zeros(no,1);
    w = zeros(no,1);

for i = 1:1:no
    Tc_CO2 = 304.12;                  % K
    Tc_MeOH = 440.911468;             % K
    Pc_CO2 = 7374000;                 % Pa
    Pc_MeOH = 6509287.85;      % Pa
    Vc_CO2 = .094*(10^-3);            % m^3/mol
    Vc_MeOH  = 0.10966*(10^-3);     % m^3/mol
    w_CO2    = .22;
    w_MeOH   = 0.50547735;
    Mw_CO2   = 44;
    Mw_MeOH = 32.04216;
    %---------------------------------------------------------------
    % MeOH + Water for cosolvent
    Tc_H2O = 647.096;                 %K
    Pc_H2O = 22064000 ;               %Pa
    Vc_H2O = 0.0559478*(10^-3);       %m^3/mol
    Mw_H2O = 18.0153 ;
    w_H2O = 0.344861;
    %---------------------------------------------------------------
    MeOH_percent = 80 ;                     %v/v of MeOH for cosolvent
    H2O_percent = 100-MeOH_percent;   % v/v of H2O for cosolvent
    y_H2O = 1-(MeOH_percent/100);     % mole fraction
    y_MeOH = MeOH_percent/100;              % mole fraction

    %------------Mixed between cosolvent: MeOH Vs Water--------------
    Tc_MeOHco = Tc_MeOH*y_MeOH+Tc_H2O*y_H2O;        %K
    Pc_MeOHco = Pc_MeOH*y_MeOH+Pc_H2O*y_H2O;        %Pa
    Vc_MeOHco = Vc_MeOH*y_MeOH+Vc_H2O*y_H2O;        %m^3/mol
    w_MeOHco =  w_MeOH*y_MeOH+w_H2O*y_H2O;

    %For input wt % of cosolvent in solvent
    MeOHco_percent = 7.8;                                      % wt %
    CO2_percent   = 100 - MeOHco_percent;                       % wt %
    MeOHco_ratio = MeOHco_percent/Mw_MeOH ;
    CO2_ratio = CO2_percent /Mw_CO2 ;
    y_MeOHco = MeOHco_ratio/(MeOHco_ratio+CO2_ratio);
    y_CO2   = 1-y_MeOHco;

    % subscript 1: supercritical fluids and subscript 2: solute
    Tc(1)  = Tc_CO2*y_CO2+Tc_MeOHco*y_MeOHco;       %K
    Tc(2)  = 1496.907;                                   %K
    Pc(1)  = Pc_CO2*y_CO2+Pc_MeOHco*y_MeOHco;        % Pa
```

```
    Pc(2) = 4035882;      %Gani method
    Vc(1) = Vc_CO2*y_CO2+Vc_MeOHco*y_MeOHco;       % m^3/mol
    Vc(2) = 0.778*(10^-3);        %Gani method  m^3/mol
    w(1) =  w_CO2*y_CO2+w_MeOHco*y_MeOHco;
    w(2) =  1.594;          %LKP
    neta = 0; %Ind. Eng. Chem. Vol.22, no. 4 1983

   % Define Psub-the sublimation pressure of the condensed phase (Pa).
    delZb = 0.97;
    Kf = 1.3;
    delSb = Kf*(8.75+1.987*log(Tb));
    % above eq. use R = 1.987 cal/mol-K (only for Psub estimation)
    Trb = T/Tb;
    if Trb > 0.5
        if Trb < 0.6
            m = 0.8;
        else
            m = 0.36;
        end
    else
        m = 1.19;
    end
    gr = 1-((3-2*Trb)^m)/Trb-2*m*((3-2*Trb)^(m-1))*log(Trb);
    Psub = (exp(delSb/1.987/delZb*gr))*760*0.00133322*100000;

    P = 0;
    Pc1 = Pc(1);    %Pa
    i = 0;

    for m =1:1:7
        P = m*10000000
          i = round(1*m);
        Pr(i) = P/1000000; % vary operating pressure (MPa)

    options = optimset( ...          %%% defaults  %%%
        'MaxFunEvals'     ,  100000000,...
        'MaxIter'         ,  100000000,...
        'TolCon'          ,  1e-100,...
        'TolFun'          ,  1e-100, ...             % 1e-6
        'TolX'            ,  1e-100);                % 1e-6
    %     'Diagnostics'     , 'on'   , ...               % 'off'
    %     'Display'         , 'iter' , ...               % 'final'
    %     'LargeScale'      , 'on'   , ...               % 'off'
    %     'MaxPCGIter'      ,  200   , ...               % n/2
    %     'PrecondBandWidth',  inf   , ...               % 0

    format long

    % Make a starting guess at the solution
    y0 = [10^-3; 10^-8];

% Calculate the solubility from six equations of state.

    % Lee-Kesler-Plocker Equation of State (LKP-EOS)
    [yl] = fsolve(@LKP,y0,options,no,T,vs,Tb,Tc,Pc,Vc,w,neta,P,Psub);
    ylkp(i) = log10(yl(1));

    % Mohsennia Modarres Mansoori Equation of State (MMM-EOS)
    [ym] = fsolve(@MMM,y0,options,no,T,vs,Tb,Tc,Pc,Vc,w,neta,P,Psub);
    ymmm(i) = log10(ym(1));

    % Peng Robinson Equation of State (PR-EOS)
    [yp] = fsolve(@PR,y0,options,no,T,vs,Tb,Tc,Pc,Vc,w,neta,P,Psub);
    yPeng(i) = log10(yp(1));

    % Redlich-Kwong Equation of State (RK-EOS)
    [yrk] = fsolve(@RK,y0,options,no,T,vs,Tb,Tc,Pc,Vc,w,neta,P,Psub);
```

```
    yRK(i) = log10(yrk(1));

    % van der Waals Equation of State (vdW-EOS)
    [yv] = fsolve(@vdW,y0,options,no,T,vs,Tb,Tc,Pc,Vc,w,neta,P,Psub);
    yvdW(i) = log10(yv(1));

    % Soave Redlich Kwong Equation of State (SRK-EOS)
    [ysrk] =fsolve(@SRK,y0,options,no,T,vs,Tb,Tc,Pc,Vc,w,neta,P,Psub);
    ySRK(i) = log10(ysrk(1));

    end
    cftool(Pr,ySRK)
    cftool(Pr,yvdW)
    cftool(Pr,yRK)
    cftool(Pr,yPeng)
    cftool(Pr,ylkp)
    cftool(Pr,ymmm)
```

B.2 MATLAB Commands for Obtaining Fugacity Coefficients

van der Waals Equation of State (vdW-EOS)

```
% vdW.m : calculates fugacity coefficient with vdW-EOS
% Parameters:
% T: Temperature [=] K
% P: Presure [=] Pa
% Tc: critical temperature [=] K
% Pc: critical presure [=] Pa
% w: accentric factor
% Psub: sublimation pressure [=] Pa

function [F] = vdW(y,no,T,vs,Tb,Tc,Pc,Vc,w,neta,P,Psub);

R = 8.314; % gas constant:  J/(mol K)
% Define some parameters
a  = zeros(2,2);
b  = zeros(2,2);
% Reduced variables and Parameters of the EOS for a pure component
for i=1:2
    a(i,i) = 27*(R*Tc(i))^2/(64*Pc(i));
    b(i,i) = R*Tc(i)/(8*Pc(i));
end
for i=1:2
    if i < 2
        a(i,i+1) = (a(i,i)*a(i+1,i+1))^.5;
        b(i,i+1) = (b(i,i)+b(i+1,i+1))/2;
    else
        a(i,i-1) = a(i-1,i);
        b(i,i-1) = b(i-1,i);
    end
end
% x is a mole fraction in gas phase and x(1)+x(2)=1
% y(1) = x(2) and y(2) = fugacity coefficient of component 2
x(2) = y(1);
x(1) = 1-x(2);

am = 0;
bm = 0;
am1 = 0;
bm1 = 0;
for i=1:2
    for j=1:2
        am = am+x(i)*x(j)*a(i,j);
        bm = bm+x(i)*x(j)*b(i,j);
    end
    am1 = am1+x(i)*a(2,i);
    bm1 = bm1+x(i)*b(2,i);
end
```

```
% Compressibility factor
c1 = 1;
c2 =-bm-(R*T/P);
c3 =(am/P);
c4 =-(am*bm/P);
GG = roots([c1 c2 c3 c4]);

j = 1;
zee=[];
for i =1:3
    if imag(GG(i))==0;
       zee(j)=GG(i);
       j = j+1;
    end
end

z = min(zee);
Treal = T
Preal = P
v = R*T*z/P   % unit: m3/gmol

%V0 = R*T/P;
%options = optimset( ...                              %%%  defaults  %%%
%     'MaxFunEvals'     ,  1000000,...
%     'MaxIter'         ,  1000000,...
%     'TolCon'          ,  1e-1000000,...
%     'TolFun'          ,  1e-1000000, ...                  % 1e-6
%     'TolX'            ,  1e-1000000);                     % 1e-6
%     'Diagnostics'     , 'on'    , ...                     % 'off'
%     'Display'         , 'iter'  , ...                     % 'final'
%     'LargeScale'      , 'on'    , ...                     % 'off'
%     'MaxPCGIter'      ,  200    , ...                     % n/2
%     'PrecondBandWidth',  inf    , ...                     % 0
%F1= @(Vrm)(Vrm^3)*c1+(Vrm^2)*c2+Vrm*c3+c4;
%v = fsolve(F1,V0,options);

% Fugacity coefficient
s1 = b(2,2)/(v-bm) ;
s2 = -log(z*(1-(bm/v))) ;
s3 = -2*am1/(R*T*v);
fhi = exp(s1+s2+s3);
%if isreal(fhi)
    %density=P*MW/(Z*R*T);
 %   result = [Z v fhi];
%else
 %   'No real solution for "fhi" is available in this phase'
  %  result=['N/A' 'N/A' 'N/A'];
%end

%solubility eq.
rs2 = Psub/P*(exp(vs*(P-Psub)/(R*T)));
E=fhi-rs2/y(1)
F=[fhi-rs2/y(1)
   y(2)-fhi];
```

Soave Redlich Kwong Equation of State (SRK-EOS)

```
% SRK.m : calculates fugacity coefficient with SRK-EOS
% Parameters:
% T: Temperature [=] K
% P: Presure [=] Pa
% Tc: critical temperature [=] K
% Pc: critical presure [=] Pa
% w: accentic factor
% Psub: sublimation pressure [=] Pa

function [F] = SRK(y,no,T,vs,Tb,Tc,Pc,Vc,w,neta,P,Psub);
```

```
R = 8.314; % gas constant : J/(mol K)

% Define some parameters
a   = zeros(2,2);
b   = zeros(2,2);
m   = zeros(2,1);
alfa = zeros(2,1);
A   = zeros(2,2);
B   = zeros(2,2);
% Reduced variables and Parameters of the EOS for a pure component
for i=1:2
    m(i) = 0.48 + 1.574*w(i) - 0.176*w(i)^2;
    alfa(i) = (1 + m(i)*(1 - sqrt(T/Tc(i))))^2;
end

for i=1:2
    a(i,i) = alfa(i)*0.42747*(R*Tc(i))^2/Pc(i);
    b(i,i) = 0.08664*R*Tc(i)/Pc(i);
end
for i=1:2
    if i < 2
        a(i,i+1) = (a(i,i)*a(i+1,i+1))^.5;
        b(i,i+1) = (b(i,i)+b(i+1,i+1))/2;
    else
        a(i,i-1) = a(i-1,i);
        b(i,i-1) = b(i-1,i);
    end
end

% x is a mole fraction in gas phase and x(1)+x(2)=1
% y(1) = x(2) and y(2) = fugacity coefficient of component 2
x(2) = y(1);
x(1) = 1-x(2);

am = 0;
bm = 0;
am1 = 0;
am2 = 0;
for i=1:2
    for j=1:2
        am = am+x(i)*x(j)*a(i,j);
        bm = bm+x(i)*x(j)*b(i,j);
    end
    am1 = am1+x(i)*a(2,i);
    am2 = am2+x(i)*(a(2,i)^0.5);
end
    A = am*P/((R*T)^2);
    B = bm*P/(R*T);

% Compressibility factor
c1 = 1;
c2 = -1;
c3 = A-B-(B^2);
c4 = -A*B;
GG = roots([c1 c2 c3 c4]);

j = 1;
zee=[];
for i =1:3
    if imag(GG(i))==0;
      zee(j)=GG(i);
      j = j+1;
    end
end

z = min(zee);
```

```
Treal = T
Preal = P
v = R*T*z/P   % unit: m3/gmol

%V0 = R*T/P;
%options = optimset( ...                              %%%  defaults  %%%
%     'MaxFunEvals'     ,  1000000,...
%     'MaxIter'         ,  1000000,...
%     'TolCon'          ,  1e-1000000,...
%     'TolFun'          ,  1e-1000000, ...               % 1e-6
%     'TolX'            ,  1e-1000000);                  % 1e-6
%     'Diagnostics'     , 'on'   , ...                  % 'off'
%     'Display'         , 'iter' , ...                  % 'final'
%     'LargeScale'      , 'on'   , ...                  % 'off'
%     'MaxPCGIter'      ,  200   , ...                  % n/2
%     'PrecondBandWidth',  inf   , ...                  % 0
%F1= @(Vrm)(Vrm^3)*c1+(Vrm^2)*c2+Vrm*c3+c4;

%v = fsolve(F1,V0,options);

% Fugacity coefficient
s1 = -log(z-B) ;
s2 = (z-1)*b(2,2)/bm;
s3 = (2*(a(2,2)^0.5)*am2/am-(b(2,2)/bm));
s4 = -am*(log(1+(bm/v)))/(bm*R*T);
fhi = exp(s1+s2+s3*s4);
%if isreal(fhi)
    %density=P*MW/(Z*R*T);
 %   result = [Z v fhi];
%else
 %   'No real solution for "fhi" is available in this phase'
  %  result=['N/A' 'N/A' 'N/A'];
%end

% Solubility eq.
rs2 = Psub/P*(exp(vs*(P-Psub)/(R*T)));
E=fhi-rs2/y(1)
F=[fhi-rs2/y(1)
      y(2)-fhi];
```

Redlich-Kwong Equation of State (RK-EOS)

```
% RK.m : calculates fugacity coefficient with RK-EOS
% Parameters:
% T: Temperature [=] K
% P: Presure [=] Pa
% Tc: critical temperature [=] K
% Pc: critical presure [=] Pa
% w: accentic factor
% Psub: sublimation pressure [=] Pa

function [F] = RK(y,no,T,vs,Tb,Tc,Pc,Vc,w,neta,P,Psub);

R = 8.314; % gas constant:  J/(mol K)

% Define some parameters
a  = zeros(2,2);
b  = zeros(2,2);
% Reduced variables and Parameters of the EOS for a pure component

for i=1:2
    a(i,i)  = 0.42748*(R^2)*((Tc(i))^2.5)/Pc(i);
    b(i,i)  = 0.08664*R*Tc(i)/Pc(i);
end
for i=1:2
    if i < 2
        a(i,i+1)  = (a(i,i)*a(i+1,i+1))^.5;
        b(i,i+1)  = (b(i,i)+b(i+1,i+1))/2;
```

```
    else
        a(i,i-1) = a(i-1,i);
        b(i,i-1) = b(i-1,i);
    end
end

% x is a mole fraction in gas phase and x(1)+x(2)=1
% y(1) = x(2) and y(2) = fugacity coefficient of component 2
x(2) = y(1);
x(1) = 1-x(2);

am = 0;
bm = 0;
a1 = 0;
b1 = 0;
for i=1:2
    for j=1:2
        am = am+x(i)*x(j)*a(i,j);
        bm = bm+x(i)*x(j)*b(i,j);
    end
    b1 = b1+x(i)*b(2,i);
    a1 = a1+x(i)*a(2,i);
end
aa=am
bb=bm
a11=a1
A = am*P/((R^2)*(T^2.5));
B = bm*P/(R*T);

c1 = 1;
c2 =-1;
c3 = A-B-(B^2);
c4 = -A*B;
% Compressibility factor
GG = roots([c1 c2 c3 c4]);

j = 1;
zee=[];
for i =1:3
    if imag(GG(i))==0;
       zee(j)=GG(i);
       j = j+1;
    end
end

z = min(zee)
Treal = T
Preal = P
v = R*T*z/P   % unit: m3/gmol

%V0 = R*T/P;
%options = optimset( ...                          %%%  defaults  %%%
%    'MaxFunEvals'     ,  1000000,...
%    'MaxIter'         ,  1000000,...
%    'TolCon'          ,  1e-1000000,...
%    'TolFun'          ,  1e-1000000, ...               % 1e-6
%    'TolX'            ,  1e-1000000);                  % 1e-6
%    'Diagnostics'     , 'on'   , ...                  % 'off'
%    'Display'         , 'iter' , ...                  % 'final'
%    'LargeScale'      , 'on'   , ...                  % 'off'
%    'MaxPCGIter'      ,  200   , ...                  % n/2
%    'PrecondBandWidth',  inf   , ...                  % 0
%F1= @(Vrm)(Vrm^3)*c1+(Vrm^2)*c2+Vrm*c3+c4;

%v = fsolve(F1,V0,options);

% Fugacity coefficient
```

```
s1 = b(2,2)*(z-1)/bm ;

s2 = -log(z*(1-(bm/v))) ;
s3 = (log(1+(bm/v)))/(R*bm*(T^1.5)) ;
s4 = (am*b(2,2)/bm)-2*a1 ;
fhi = exp(s1+s2+s3*s4);

 if isreal(fhi)
     density=P*MW/(Z*R*T);
     result = [Z v fhi];
else
     'No real solution for "fhi" is available in this phase'
     result=['N/A' 'N/A' 'N/A'];
end

% Solubility eq.
rs2 = Psub/P*(exp(vs*(P-Psub)/(R*T)));
E=fhi-rs2/y(1)
F=[fhi-rs2/y(1)
   y(2)-fhi];
```

Mohsennia Modarres Mansoori Equation of State (MMM-EOS)

```
% MMM.m : calculates fugacity coefficient with MMM-EOS
% Parameters:
% T: Temperature [=] K
% P: Presure [=] Pa
% Tc: critical temperature [=] K
% Pc: critical presure [=] Pa
% w: accentic factor
% Psub: sublimation pressure [=] Pa

function [F] = MMM(y,no,T,vs,Tb,Tc,Pc,Vc,w,neta,P,Psub)

R = 8.314;
a = zeros(no,no);
b = zeros(no,no);
for i=1:no
    a(i,i) = .48748*(R^2)*(Tc(i)^2.5)/Pc(i);
    b(i,i) = .064662*R*Tc(i)/Pc(i);
end
for i=1:no
    if i < no
        a(i,i+1) = (a(i,i)*a(i+1,i+1))^.5;
        b(i,i+1) = 1/8*(((b(i,i)^(1/3))+(b(i+1,i+1)^(1/3)))^3);
    else
        a(i,i-1) = a(i-1,i);
        b(i,i-1) = b(i-1,i);
    end
end
am = 0;
bmi = 0;
bmj = 0;
% x is a mole fraction in gas phase and x(1)+x(2)=1
% y(1) = x(2) and y(2) = fugacity coefficient of component 2
x(2) = y(1);
x(1) = 1-x(2);

b1 = 0;
b2 = 0;
a1 = 0;
for i=1:no
    for j=1:no
        am = am+x(i)*x(j)*a(i,j);
        bmi = bmi+3*x(i)*x(j)*b(i,j);
        b2 = b2+x(i)*x(j)*b(i,j);
    end
    bmj = bmj+x(i)*b(i,i);
```

```
    b1 = b1+x(i)*b(2,i);
    a1 = a1+x(i)*a(2,i);
end
bm = 1/4*(bmi+bmj);

bmc = 1.3191*bm;
amc = am/(R*(T^1.5));
rtc = R*T/P;

c1 = (rtc^2);
c2 = rtc*(bmj-bm)-(rtc^2);
c3 = -bm*bmj-rtc*(bmj+bmc-amc);
c4 = -(bmc*bmj+amc*bm);

GG = roots([c1 c2 c3 c4]);

j = 1;
zee=[];
for i =1:3
    if imag(GG(i))==0;
       zee(j)=GG(i);
       j = j+1;
    end
end

z = min(zee);
Treal = T
Preal = P
v = R*T*z/P   % unit: m3/gmol

%V0 = R*T/P;
%options = optimset( ...                                %%%  defaults  %%%
%     'MaxFunEvals'     ,  1000000,...
%     'MaxIter'         ,  1000000,...
%     'TolCon'          ,  1e-1000000,...
%     'TolFun'          ,  1e-1000000, ...                 % 1e-6
%     'TolX'            ,  1e-1000000);                    % 1e-6
%     'Diagnostics'     , 'on'   , ...                    % 'off'
%     'Display'         , 'iter' , ...                    % 'final'
%     'LargeScale'      , 'on'   , ...                    % 'off'
%     'MaxPCGIter'      ,  200   , ...                    % n/2
%     'PrecondBandWidth',  inf   , ...                    % 0
%F1= @(Vrm)(Vrm^3)*c1+(Vrm^2)*c2+Vrm*c3+c4;

%v = fsolve(F1,V0,options);

% fugacity co. eq.
s1 = 2.3191*((3*(2*b1-b2)+b(2,2))/(4*(v-bm))-(log(1-bm/v)))-log(z);
s2 = am/(R*(T^1.5)*bmj);
s3 = (b(2,2)/bmj-2*a1/am)*(log(1+bmj/v))-b(2,2)/(v+bmj);

lfug = s1+s2*s3;
elfug = exp(s1+s2*s3);

% solubility eq.
rs2 = Psub/P*(exp(vs*(P-Psub)/(R*T)));

F=[elfug-rs2/y(1)
     y(2)-elfug];
```

Peng Robinson Equation of State (PR-EOS)

```
% PR.m : calculates the fugacity coefficient with PR-EOS
% Parameters:
% T: Temperature [=] K
% P: Presure [=] Pa
% Tc: critical temperature [=] K
% Pc: critical presure [=] Pa
```

```
% w: acentric factor
% Psub: sublimation pressure [=] Pa

function [F] = PR(y,no,T,vs,Tb,Tc,Pc,Vc,w,neta,P,Psub);

R = 8.314; % gas constant: J/(mol K)

% Define some parameters
a   = zeros(2,2);
b   = zeros(2,2);
m   = zeros(2,1);
alfa = zeros(2,1);
A   = zeros(2,2);
B   = zeros(2,2);
% Reduced variables and Parameters of the EOS for a pure component
for i=1:2
    m(i) = 0.37464 + 1.54226*w(i) - 0.26992*w(i)^2;
    alfa(i) = (1 + m(i)*(1 - sqrt(T/Tc(i))))^2;
end

for i=1:2
    a(i,i) = alfa(i)*0.45724*(R*Tc(i))^2/Pc(i);
    b(i,i) = 0.0778*R*Tc(i)/Pc(i);
end
for i=1:2
    if i < 2
        a(i,i+1) = (a(i,i)*a(i+1,i+1))^.5;
        b(i,i+1) = (b(i,i)+b(i+1,i+1))/2;
    else
        a(i,i-1) = a(i-1,i);
        b(i,i-1) = b(i-1,i);
    end
end

% x is a mole fraction in gas phase and x(1)+x(2)=1
% y(1) = x(2) and y(2) = fugacity coefficient of component 2
x(2) = y(1);
x(1) = 1-x(2);

am = 0;
bm = 0;
am1 = 0;

for i=1:2
    for j=1:2
        am = am+x(i)*x(j)*a(i,j);
        bm = bm+x(i)*x(j)*b(i,j);
    end
    am1 = am1+x(i)*a(2,i);
end
    A = am*P/(R*T)^2;
    B = bm*P/(R*T);

c1 = 1;
c2 =-(1-B);
c3 =(A-3*B^2-2*B);
c4 =-(A*B-B^2-B^3);

% Compressibility factor

GG = roots([c1 c2 c3 c4]);

j = 1;
zee=[];
for i =1:3
    if imag(GG(i))==0;
       zee(j)=GG(i);
       j = j+1;
    end
end

z = min(zee);
Treal = T
Preal = P
v = R*T*z/P   % unit: m3/gmol

%V0 = R*T/P;
```

```
%options = optimset( ...                          %%%  defaults  %%%
%     'MaxFunEvals'      ,  1000000,...
%     'MaxIter'          ,  1000000,...
%     'TolCon'           ,  1e-1000000,...
%     'TolFun'           ,  1e-1000000, ...                %  1e-6
%     'TolX'             ,  1e-1000000);                   %  1e-6
%     'Diagnostics'      , 'on'    , ...                  % 'off'
%     'Display'          , 'iter'  , ...                  % 'final'
%     'LargeScale'       , 'on'    , ...                  % 'off'
%     'MaxPCGIter'       ,  200    , ...                  % n/2
%     'PrecondBandWidth',  inf    , ...                  % 0
%F1= @(Vrm)(Vrm^3)*c1+(Vrm^2)*c2+Vrm*c3+c4;

%v = fsolve(F1,V0,options);

% Fugacity coefficient
s1 = (z-1)*b(2,2)/bm ;
s2 = -log(z-B) ;
s3 = -A/(2*(sqrt(2))*B) ;
s4 = (2*am1/am)-(b(2,2)/bm) ;
s5 = log((z+(1+sqrt(2))*B)/(z+(1-sqrt(2))*B)) ;
fhi = exp(s1+s2+s3*s4*s5);
%if isreal(fhi)
    %density=P*MW/(Z*R*T);
 %   result = [Z v fhi];
%else
 %   'No real solution for "fhi" is available in this phase'
  %  result=['N/A' 'N/A' 'N/A'];
%end

%solubility eq.
rs2 = Psub/P*(exp(vs*(P-Psub)/(R*T)));
E=fhi-rs2/y(1)
F=[fhi-rs2/y(1)
   y(2)-fhi];
```

Lee-Kesler-Plocker Equation of State (LKP-EOS)

```
% LKP.m : calculates the fugacity coefficient with LKP-EOS
% Parameters:
% T: Temperature [=] K
% P: Presure [=] Pa
% Tc: critical temperature [=] K
% Pc: critical presure [=] Pa
% w: accentic factor
% Psub: sublimation pressure [=] Pa

function [F] = LKP(y,no,T,vs,Tb,Tc,Pc,Vc,w,neta,P,Psub)

R = 8.314;
% define the cross coefficients
Tcc = zeros(no,no);
Pcc = zeros(no,no);
for i=1:no
    for j=1:no
        Tcc(i,j) = (Tc(i)*Tc(j))^.5;
        Vcc(i,j) = (((Vc(i)^(1/3))+(Vc(j)^(1/3)))^3)/8;
    end
end

% define two universal sets of constants for the LK EOS
bo1 = .1181193;
br1 = .2026579;
bo2 = .265728;
br2 = .331511;
bo3 = .154790;
br3 = .027655;
bo4 = .030323;
br4 = .203488;
co1 = .0236744;
cr1 = .0313385;
co2 = .0186984;
cr2 = .0503618;
```

```
co3 = .0;
cr3 = .016901;
co4 = .042724;
cr4 = .041577;
do1 = .155428*(10^-4);
dr1 = .48736*(10^-4);
do2 = .623689*(10^-4);
dr2 = .0740336*(10^-4);
beo = .65392;
ber = 1.226;
gao = .060167;
gar = .03754;
wr = .3978;

% x is a mole fraction in gas phase and x(1)+x(2)=1
% y(1) = x(2) and y(2) = fugacity coefficient of component 2
x(2) = y(1);
x(1) = 1-x(2);

Vcm = 0;
Tcm = 0;
Tcmm = 0;
wm = 0;
for i=1:no
    for j=1:no
        Vcm = Vcm+Vcc(i,j)*x(i)*x(j);
        Tcmm = Tcmm+Tcc(i,j)*x(i)*x(j)*(Vcc(i,j)^neta);
    end
    wm = wm+x(i)*w(i);
end
Tcm = Tcmm/(Vcm^neta);
Pcm = (.2905-.085*wm)*R*Tcm/Vcm;
Zcm = (.2905-.085*wm);
Trm = T/Tcm;
Prm = P/Pcm;

V0 = Zcm*R*T/P/Vcm;

%for simple fluid cal. specific volume, Z, fugacity coeff. and...
%Isothermal Enthalpy Departure.
B = bo1 - bo2/Trm - bo3/Trm^2 - bo4/Trm^3;
C = co1 - co2/Trm + co3/Trm^3;
D = do1 + do2/Trm;
cc = co4;
bbe = beo;
gga = gao;
options = optimset( ...                                  %%%  defaults  %%%
    'MaxFunEvals'     ,  1000000,...
    'MaxIter'         ,  1000000,...
    'TolCon'          ,  1e-1000000,...
    'TolFun'          ,  1e-1000000, ...                       % 1e-6
    'TolX'            ,  1e-1000000);                          % 1e-6
%     'Diagnostics'     , 'on'    , ...                        % 'off'
%     'Display'         , 'iter'  , ...                        % 'final'
%     'LargeScale'      , 'on'    , ...                        % 'off'
%     'MaxPCGIter'      ,  200    , ...                        % n/2
%     'PrecondBandWidth',  inf    , ...                        % 0

F1= @(Vrm)Vrm-Trm/Prm-B*Trm/Prm/Vrm-C*Trm/Prm/(Vrm^2)-D*Trm/Prm/(Vrm^5)-...
    Trm/Prm*cc/((Trm^3)*(Vrm^2))*(bbe+gga/(Vrm^2))*exp(-gga/(Vrm^2));
Vorm = fsolve(F1,V0,options);
Zorm = Prm*Vorm/Trm;
E = co4/gao/2/(Trm^3)*(beo+1-(beo+1+gao/(Vorm^2))*exp(-gao/(Vorm^2)));
lnfom = Zorm-1-log(Zorm)+B/Vorm+C/2/(Vorm^2)+D/5/(Vorm^5)+E;
%define dH/RTc -> dH
dHom = Trm*(Zorm-1-(bo2+2*bo3/Trm+3*bo4/(Trm^2))/Trm/Vorm-...
      (co2-3*co3/(Trm^2))/2/Trm/(Vorm^2)+do2/5/Trm/(Vorm^5)+3*E);
```

```
%for reference fluid cal. specific volume, Z, fugacity coeff. and...
%Isothermal Enthalpy Departure.
B = br1 - br2/Trm - br3/Trm^2 - br4/Trm^3;
C = cr1 - cr2/Trm + cr3/Trm^3;
D = dr1 + dr2/Trm;
cc = cr4;
bbe = ber;
gga = gar;
F2= @(Vrm)Vrm-Trm/Prm-B*Trm/Prm/Vrm-C*Trm/Prm/(Vrm^2)-D*Trm/Prm/(Vrm^5)-...
    Trm/Prm*cc/((Trm^3)*(Vrm^2))*(bbe + gga/(Vrm^2))*exp(-gga/(Vrm^2));
Vrrm = fsolve(F2,V0,options);
Zrrm = Prm*Vrrm/Trm;
E = cr4/gar/2/(Trm^3)*(ber+1-(ber+1+gar/(Vrrm^2))*exp(-gar/(Vrrm^2)));
lnfrm = Zrrm-1-log(Zrrm)+B/Vrrm+C/2/(Vrrm^2)+D/5/(Vrrm^5)+E;
%define dH/RTc -> dH
dHrm = Trm*(Zrrm-1-(br2+2*br3/Trm+3*br4/(Trm^2))/Trm/Vrrm-...
      (cr2-3*cr3/(Trm^2))/2/Trm/(Vrrm^2)+do2/5/Trm/(Vrrm^5)+3*E);
%total
Zm = (Zrrm-Zorm)*wm/wr+Zorm
Vm = (Vrrm-Vorm)*wm/wr+Vorm
lnfm = (lnfrm-lnfom)*wm/wr+lnfom;
dHm = (dHrm-dHom)*wm/wr+dHom;
zabs = abs(Zm);
%define equation for fugacity coeff. of component 2
t5 = 0;
t7 = 0;
for i=1:no
    t5 = t5+x(i)*(Vcc(i,1)-Vcc(i,2));
    t7 = t7+x(i)*((Vcc(i,1)^neta)*Tcc(i,1)-(Vcc(i,2)^neta)*Tcc(i,2));
end
t5 = 2*t5;
t7 = 2*t7;
t1 = (t7-(neta*(Vcm^(neta-1))*t5*Tcm))/(Vcm^neta);
t4 = w(1)-w(2);
t6 = -.085*t4;
t2 = Pcm*(t6/Zcm+t1/Tcm-t5/Vcm);
t3 = (lnfrm-lnfom)/wr;
lfug = lnfm-dHm/T*x(1)*t1+(Zm-1)/Pcm*x(1)*t2-t3*x(1)*t4;

% solubility eq.
rs2 = Psub/P*(exp(vs*(P-Psub)/(R*T)));

F=[y(1)-rs2/y(2)
   y(2)-exp(lfug)];
```

B.3 Gproms Code for Obtaining the Yield in the SFE process

```
DECLARE
 TYPE
   Type1 = 1 : -1E6 : 1E6 UNIT = "m" # Axial position
   Type2 = 1 : -1E6 : 1E6 UNIT = "m" # Radial position
   Type3 = 1 : -1E6 : 1E6 UNIT = "mol/m3" # Concentration
   Type4 = 1 : -1E6 : 1E6 UNIT = "Pa" # Partial pressures
   Type5 = 1 : -1E6 : 1E6 UNIT = "K" # Temperature
   Type6 = 1 : -1E6 : 1E6 UNIT = "mol/kg.s.Pa2" # Reaction constant
   Type7 = 1 : -1E6 : 1E6 UNIT = "mol/kg.s" # Reaction rate
   Type8 = 1 : -1E6 : 1E6 UNIT = "mol/m3" # Feed concentration
   Type9 = 1 : -1E6 : 1E6 UNIT = "Pa" # Feed partial pressures
   Type10 = 1 : -1E6 : 1E6 UNIT = "K" # Feed temperature
   Type11 = 1 : -1E6 : 1E6 UNIT = "m/s" # Superficial gas velocity
   Type12 = 1 : -1E6 : 1E6 UNIT = "m/s" # Coolant flow rate
   Type13 = 1 : -1E6 : 1E6 UNIT = "K" # Coolant temperature
   Type14 = 1 : -1E6 : 1E6 UNIT = "K" # Coolant inlet temperature
   Type15 = 1 : -1E6 : 1E6 UNIT = "W" # Total heat load absorbed by coolant
END # Declare

#------------------------------------------------------------
                              Model description of SFE
```

```
#-----------------------------------------------------------
MODEL SCM
PARAMETER
   L           AS INTEGER # Fixed Bed Length
   R           AS REAL # Fixed Bed Radius
   Rc          AS REAL # Initial Core Radius
   dp          AS REAL # Particle size
   rhom        AS REAL # Mixture density
   rhob        AS INTEGER # Bed density
   rhof        AS REAL # Fluid density
   vf          AS REAL # Fluid velocity
   DAB         AS REAL # Binary diffusion coefficient
   DAL         AS REAL # Axial diffusivity
   kf          AS REAL # mass transfer coefficient
   BedVoid     AS REAL # Bed voidage fraction
   Epsilon     As REAL # Solid porosity
   No          AS INTEGER # Number of components present
   q0          AS REAL # Maximum solute concentration
   Csat        AS REAL # Solubility
   w           AS REAL # Solid weight

DISTRIBUTION_DOMAIN

  Axial AS (0:L)
  Radial AS (0:R)

VARIABLE
 Xb            AS DISTRIBUTION(No,Axial,Radial) OF Type3 # Bulk solute Concentration
 rc            AS DISTRIBUTION(No,Axial,Radial) OF Type4 # Core radius
 a             AS Type5 #
 b             AS Type6 #
 Bi            AS Type7 #
 Pe            AS Type8 #
 Sh            AS Type9 #
 Re            AS Type10 #
 Sc            AS Type11 #

BOUNDARY
# Boundary condition at reactor entrance (z = 0)
FOR r := 0 TO R DO
 PARTIAL(Xb(,0,r),Axial) = Pe*Xb(,0,r);
END #For

# Boundary condition at reactor exit (z = L)
FOR r := 0 TO R DO
 PARTIAL(Xb(,L,r),Axial) = 0;
END #For

# Boundary condition at reactor centre (r = 0)
FOR z := 0|+ TO L|- DO
 PARTIAL(Xb(,z,0),Radial) = 0;
END #For

# Boundary condition at reactor perimeter (r = R)
FOR z := 0|+ TO L|- DO
 PARTIAL(Xb(,z,R),Radial) = 0;
END #For

EQUATION

        dp = Rp*2
        A  = pi*R^2;
        vf = Q/A;
        Re = dp*vf*rhom/mu;
        Sc = mu/(rhom*DAB);
        b = Csat/q0;
        Sc = mu/(rhom*DAB);
        b = Csat/q0;

# Axial dispersion coefficient

        T1 = BedVoid*Re*Sc;

        IF T1 < 0.3 THEN
          RESET DL = ((DAB*1.317)/epsilon)*(epsilon*Re*Sc)^1.392;
        ELSE
          RESET DL = 0.25*DAB/epsilon;
```

```
       END

       Pe = L*vf/DL;

# Mass Transfer Coefficient
       IF Re < 1.2918 THEN
               RESET Sh = 0.135*(Re^0.5)*(Sc^0.33);
       ELSE
         IF Re < 40 THEN
               RESET Sh = 0.38*(Re^0.83)*(Sc^0.33);
         ELSE
               RESET Sh = 2+1.1*(Re^0.6)*(Sc^0.33);
          END
       END

       kf = Sh*DAB/dp;
       Bi = kf*Rp/De;
       a = (vf*Rp^2)/(De*L);

# Component Mass Balance
FOR i := 1 TO No DO
 FOR z := 0|+ TO L|- DO
  FOR r := 0|+ TO R|- DO
   $Xb(i,i1,i2) = -a*PARTIAL(Xb(i,z,r),Axial)+(a/Pe)*PARTIAL(Xb(i,z,r),Axial,
                  Axial)+3*Bi*(1-Xb(i,z,r))/(1-Bi*(1-1/rc(i,z,r));
  END #For r
 END #For z
END #For i

# Component Core Radius Balance
FOR z := 0|+ TO L|- DO
  FOR r := 0|+ TO R|- DO
   $rc(,z,r) = Bi*(1-Xb(,z,r))/(epsilon*Bi*(Xp(,z,r)-1)+
                (1- epsilon)*b*rc(,z,r)*(rc(,z,r)+Bi*(1-rc(,z,r)));
  END #For r
 END #For z

END # Model SCM

PROCESS Sim
  UNIT
    R101 AS Fixedbed
  SET
    WITHIN R101 DO
        T := 313; #K
        P := 50; #MPa
        L := 3; # m
        R := 0.0127; # m
        dp := 0.00068; # m
        w := 100; # g
        d := 0.04; #m
        Q := 1.833*10^-6; # m3/s
        rhosl := 1663.783; # kg/m3
        rhof := 982; # kg/m3
        rhom := 974.5; # kg/m3
        Csat := 0.00794; # g solute/g solvent
        q0 := 0.1833; # g solute/g solvent
        rhom := 982; # kg/m3
        mu := 2.381*10^-4; #kg/m.s
        DAB := 7.092*10^-9; # m2/s
        BedVoid := 0.932;
        Porosity := 0.463;
        No := 1; #


# Discretisation Method
        Axial := [BFDM, 1, 50]#;
        Radial := [OCFEM, 2, 5];
    END # Within

INITIAL
 # Initial Conditions
  WITHIN R101 DO
   FOR z := 0|+ TO L|- DO
    FOR r := 0|+ TO R|- DO
     Xb(,z,r) = 0; # mol/m3;
    END #For
```

```
    END #For

    FOR z := 0|+ TO L|- DO
     FOR r := 0|+ TO R|- DO
      rc(z,r) = 1;
     END #For
    END #For
   END # Within

  SOLUTIONPARAMETERS
        ReportingInterval := 0.2;
        BlockDecomposition := ON;

  SCHEDULE
        CONTINUE FOR 4

END # Process Fixedbed

################## END OF THE PROGRAM ###################
```

CURRICULUM VITAE

NAME	Miss Thippawan Kumhom
DATE OF BIRTH	3 March 1982

EDUCATIONAL RECORD

HIGH SCHOOL	High School Graduation Seekan School, 1999
BACHELOR'S DEGREE	Bachelor of Engineering (Chemical Engineering) Suranaree University of Technology, 2004
DOCTORAL DEGREE	Doctor of Engineering (Chemical Engineering) King Mongkut's University of Technology Thonburi, 2011

RESEARCH GRANTS	The Royal Golden Jubilee Ph.D. Program, The Thailand Research Fund (Doctor's Degree).

PUBLICATIONS

Kumhom, T., Pongamphai, S., Douglas, S., Douglas, P.L. and Teppaitoon, W., 2009. "Modelling Solubility of Solids in Supercritical Fluid - Cosolvent Systems". **The 2nd Thammasat University International Conference on Chemical, Environmental and Energy Engineering (TU-CHEEE)**, March 3-4, Swissôtel Le Concorde Bangkok, Bangkok, Thailand.

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30 ก.ย. 2554

มหาวิทยาลัยเทคโนโลยีพระจอมเกล้าธนบุรี
ข้อตกลงว่าด้วยการโอนสิทธิในทรัพย์สินทางปัญญาของนักศึกษาระดับบัณฑิตศึกษา

วันที่ 7 เดือน มิถุนายน พ.ศ. 2554

ข้าพเจ้า (~~นาย/นาง~~/นางสาว) ทิพย์วรรณ คำหอม รหัสประจำตัว 49500002 เป็นนักศึกษาของ มหาวิทยาลัยเทคโนโลยีพระจอมเกล้าธนบุรี ระดับ ○ ประกาศนียบัตรบัณฑิต ○ ปริญญาโท ⊘ ปริญญาเอก หลักสูตร วิศวกรรมศาสตรดุษฎีบัณฑิต สาขาวิชา วิศวกรรมเคมี คณะวิศวกรรมศาสตร์ อยู่บ้านเลขที่ 34/922 ตรอก/ซอย รัชกร ถนน วัดไผ่เขียว ตำบล/แขวง สีกัน อำเภอ/เขต ดอนเมือง จังหวัด กรุงเทพฯ รหัสไปรษณีย์ 10210 เป็น “ผู้โอน” ขอโอนสิทธิในทรัพย์สินทางปัญญาให้ไว้กับมหาวิทยาลัยเทคโนโลยีพระจอมเกล้าธนบุรี โดยมี รศ.ดร.ปิยะบุตร วานิชพงษ์พันธุ์ ตำแหน่ง รองคณบดีฝ่ายวิชาการ คณะวิศวกรรมศาสตร์ เป็นตัวแทน “ผู้รับโอน” สิทธิในทรัพย์สินทางปัญญาและมีข้อตกลงดังนี้

1. ข้าพเจ้าได้จัดทำวิทยานิพนธ์เรื่อง แบบจำลองของกระบวนการสกัดด้วยของไหลเหนือวิกฤต ซึ่งอยู่ในความควบคุมของ รศ.ดร.สุวัสสา พงษ์อำไพ อาจารย์ที่ปรึกษา ตามพระราชบัญญัติลิขสิทธิ์ พ.ศ. 2537 และถือว่าเป็นส่วนหนึ่งของการศึกษาตามหลักสูตรของมหาวิทยาลัยเทคโนโลยีพระจอมเกล้าธนบุรี
2. ข้าพเจ้าตกลงโอนลิขสิทธิ์จากผลงานทั้งหมดที่เกิดขึ้นจากการสร้างสรรค์ของข้าพเจ้าในวิทยานิพนธ์ให้กับมหาวิทยาลัยเทคโนโลยีพระจอมเกล้าธนบุรี ตลอดอายุแห่งการคุ้มครองลิขสิทธิ์ตามพระราชบัญญัติลิขสิทธิ์ พ.ศ. 2537 ตั้งแต่วันที่ได้รับอนุมัติโครงร่างวิทยานิพนธ์จากมหาวิทยาลัย
3. ในกรณีที่ข้าพเจ้าประสงค์จะนำวิทยานิพนธ์ไปใช้ในการเผยแพร่ในสื่อใดๆ ก็ตาม ข้าพเจ้าจะต้องระบุว่าวิทยานิพนธ์เป็นผลงานของมหาวิทยาลัยเทคโนโลยีพระจอมเกล้าธนบุรีทุกครั้งที่มีการเผยแพร่
4. ในกรณีที่ข้าพเจ้าประสงค์จะนำวิทยานิพนธ์ไปเผยแพร่ หรือให้ผู้อื่นทำซ้ำหรือดัดแปลงหรือเผยแพร่ต่อสาธารณชนหรือกระทำการอื่นใด ตามพระราชบัญญัติลิขสิทธิ์ พ.ศ. 2537 โดยมีค่าตอบแทนในเชิงธุรกิจ ข้าพเจ้าจะกระทำได้เมื่อได้รับความยินยอมเป็นลายลักษณ์อักษรจากมหาวิทยาลัยเทคโนโลยีพระจอมเกล้าธนบุรีก่อน
5. ในกรณีที่ข้าพเจ้าประสงค์จะนำข้อมูลจากวิทยานิพนธ์ไปประดิษฐ์หรือพัฒนาต่อยอดเป็นสิ่งประดิษฐ์หรืองานทรัพย์สินทางปัญญาประเภทอื่น ภายในระยะเวลาสิบ (10) ปีนับจากวันลงนามในข้อตกลงฉบับนี้ ข้าพเจ้าจะกระทำได้เมื่อได้รับความยินยอมเป็นลายลักษณ์อักษรจากมหาวิทยาลัยเทคโนโลยีพระจอมเกล้าธนบุรี และมหาวิทยาลัยเทคโนโลยีพระจอมเกล้าธนบุรีมีสิทธิในทรัพย์สินทางปัญญานั้น พร้อมกับได้รับชำระค่าตอบแทนการอนุญาตให้ใช้สิทธิดังกล่าว รวมถึงการจัดสรรผลประโยชน์อันพึงเกิดขึ้นจากส่วนใดส่วนหนึ่งหรือทั้งหมดของวิทยานิพนธ์ในอนาคต โดยให้เป็นไปตามระเบียบสถาบันเทคโนโลยีพระจอมเกล้าธนบุรี ว่าด้วย การบริหารผลประโยชน์อันเกิดจากทรัพย์สินทางปัญญา พ.ศ. 2538

6. ในกรณีที่มีผลประโยชน์เกิดขึ้นจากวิทยานิพนธ์หรืองานทรัพย์สินทางปัญญาอื่นที่ข้าพเจ้าทำขึ้นโดยมีมหาวิทยาลัยเทคโนโลยีพระจอมเกล้าธนบุรีเป็นเจ้าของ ข้าพเจ้าจะมีสิทธิได้รับการจัดสรรผลประโยชน์อันเกิดจากทรัพย์สินทางปัญญาดังกล่าวตามอัตราที่กำหนดไว้ในระเบียบสถาบันเทคโนโลยีพระจอมเกล้าธนบุรี ว่าด้วย การบริหารผลประโยชน์อันเกิดจากทรัพย์สินทางปัญญา พ.ศ. 2538

ลงชื่อ ทิพย์วรรณ คำหอม ผู้โอนสิทธิ
(นางสาวทิพย์วรรณ คำหอม)
นักศึกษา

ลงชื่อ..ผู้รับโอนสิทธิ
(รศ.ดร.ปิยะบุตร วานิชพงษ์พันธุ์)
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ลงชื่อ..พยาน
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(รศ.ดร.อนวัช สังข์เพ็ชร)