

PHASE EQUILIBRIA OF HEAVY RAW PYROLYSIS GASOLINE CONTINUOUS MIXTURE USING PENG-ROBINSON EQUATION OF STATE

Sung Jae Yoo, Soo-Yong Lee* and Ki-Pung Yoo**

Dept. of Chem. Eng., Sogang University, Seoul, Korea

*Space Propulsion System Dept., Korea Aerospace Res. Inst., Daeduck Sci. Town, Taejon 305-606, Korea

(Received 29 February 1992 • accepted 15 April 1992)

Abstract—The heavy-RPG(Raw Pyrolysis Gasoline), which is a variable mixture of mainly unsaturated C_9 fractions in the cracking of petroleum naphthas, is one of the important feed materials for petroleum resins. To produce the resin with favorable quality, one need to use well purified fraction of the h-RPG and, accordingly, a knowledge of the phase equilibria for the h-RPG is required. The h-RPG, however, is regarded as a typical continuous mixture which contains far too many components for standard chemical analysis. Thus, we present here an efficient method collecting phase equilibrium data for such a mixture based the method of continuous thermodynamics and the Peng-Robinson equation of state. First, through the gas chromatographic analysis and the ASTM D86 experiment for a typical h-RPG mixture, we identified the total number of 43 constituents and found the distribution of TBPs. Then, the continuous fraction of h-RPG mixture is characterized by gamma function where the TBP index is used as the distribution variable. Finally, we performed bubble and dew point, and flash calculations by the quadrature method to the continuous fraction. The results are compared with those calculated by the pseudo-component methods. We found that the method presented here can be used for the reliable phase equilibrium calculation of such a continuous mixture while significantly reduce the computation time with more favorable accuracy over the conventional pseudocomponent method.

INTRODUCTION

The macromolecules are mixtures of molecules differing in chemical constitution and molecular size. For the purpose of establishing properties, processability, and structure relationships and of determining the polymerization mechanism by which the polymer samples are prepared, it is very important to prepare chemically well defined polymers with very narrow molecular weight distribution. To obtain chemically homologous polymers, we can consider basically two inter-related routes. As a upstream step, we need to use physicochemically well understood feed materials in the polymerization process and as a downstream step, an efficient fractionation method should be used for the synthetic polymers. While there exist various excellent fractionation techniques such as batch fractionation, gel-permeation chromatography, and ultracentrifugation [1], there are no easy way to obtain quality

controlled feed materials for the synthetic polymers when we use multicomponent feeds. Furthermore, in industrial polymerization processes, the crudly purified multicomponent monomer feeds are used frequently mainly due to the economic consideration.

One of the typical examples is the production of petroleum resins from the polymerization of h-RPG which is a variable mixture of unsaturated isomeric monomers obtained as mainly C_9 fractions in the cracking of petroleum naphthas. Worldwide, the production of petroleum resins is now about 1,000,000 tonnes/year, and that the petroleum resins have rapidly become the resin of choice in any areas- paints, printing inks, rubber compounds and adhesives and they can still be regarded as new materials-they are capable of wide development and refinement with close tailoring properties to meet the need of any application. Thus, to be the h-RPG mixture an appropriate raw feed material for the production of better qualified petroleum resins, we need a well-purified h-RPG fractions and, accordingly as a prerequisite, a reliable ther-

**To whom all correspondence should be addressed.

modynamic properties and fluid-phase equilibria for such a mixture is necessary. However, as discussed in the later section, the crude h-RPG consist of as many as of 43 C_9 constituents. Conventionally the necessary phase equilibria for such mixtures are usually computed by the pseudo-component method which intrinsically cannot avoid arbitrary lumping of the residuum composition into pseudocomponents.

For such multicomponent mixtures as the h-RPG, the composition of the h-RPG may be described by a continuous distribution function of some convenient macroscopic property such as boiling point or effective carbon number. To attain a quantitative description of phase equilibria, recently an alternative procedure called continuous thermodynamics has been presented by the authors [2-7]. An important advantage of the continuous thermodynamic framework is that it avoids arbitrary lumping process in the pseudocomponent framework.

While the continuous thermodynamics is only the logical limit of the traditional pseudocomponent methods, it is more efficient than the pseudocomponent method because it is less arbitrary and it often requires less computer time while keeping favorable accuracy. To illustrate this method, we consider a systematic computational aspect of flash problems of the h-RPG for the future improved use of the mixture in the petroleum resin industry.

EXPERIMENTAL CHARACTERIZATION OF h-RPG

The h-RPG is one of the ill-defined mixtures because it contains far too many components to permit a composition analysis for each constituent. However, it can be characterized by the separation into lumped fractions by standard distillation and chromatographic analysis.

1. ASTM D86 Distillation

To fractionally characterize the relation of vapor temperature and percentage vaporized of the h-RPG ($sp. gr. = 0.912$), the ASTM or nonfractionating distillation, and TBP test can be used in order to judge the economy of the designated separation operation. Among them, we performed the ASTM D86 distillation using a standard equipment as schematically shown in Fig. 1. We omit experimental details here and the characterization results are listed in Table 1. The ASTM D86 results are, then, converted into the TBP data by following the method presented in the API technical data book [8]. These results are shown in Fig. 2 wherein the ASTM result is compared together. The contin-

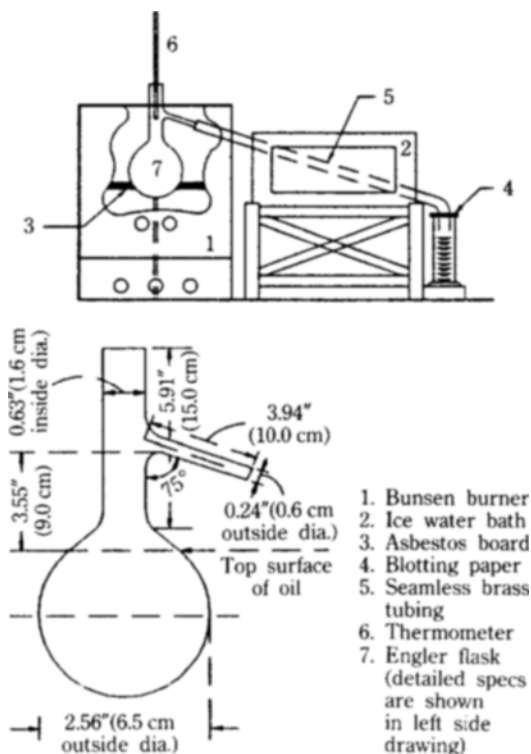


Fig. 1. Schematic drawing of the ASTM D86 distillator.

Table 1. The ASTM boiling point data for h-RPG mixture ($sp. gr. = 0.912$)

Volume distilled(%)	Temperature(K)
IBP	434.15
5	439.15
10	440.15
20	442.15
30	444.15
40	446.15
50	449.15
60	453.15
70	459.15
80	470.15
90	485.15
95	523.15
EP	531.15

uous fraction of the h-RPG is also modeled by the gamma distribution function with the mean TBP 460.414 K and variance 10741.1 as shown in Fig. 3. This gamma distribution is used later as the base feed fraction in the flash calculation.

2. Gas Chromatography

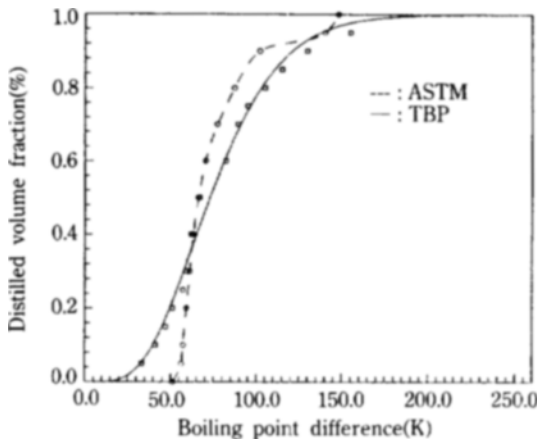


Fig. 2. The cumulative curves of ASTM and true boiling point for h-RPG.

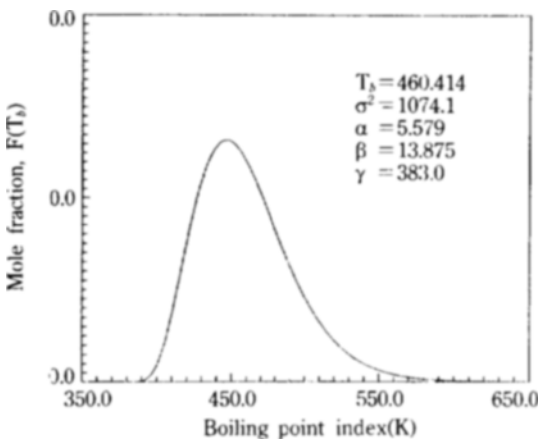


Fig. 3. The gamma distribution curve of TBP for h-RPG.

To identify the number of components contained in the h-RPG mixture, the gas chromatographic analysis is performed. In Table 2, the 43 constituents identified by the gas chromatographic analysis and their respective mole fractions and physical properties are listed. Most of the components are the C_9 monomeric isomers and the molecular weights are ranging from 66.1 to 254.4 and the TBP's from 41.0 to 372.22°C. Upon scrutiny of the distribution of the mole fractions, we selected 6 representative pseudocomponents for the h-RPG as shown in Table 3 for the later use in the pseudocomponent calculations. Also, we simply treated as the discrete components for the narrowly but complicatedly distributed portions near the initial boiling point and the end point in ASTM D86 data designated by CPD, MCPD, and TPR (Thermal Polymerized Resin) in Table 2. And the remaining whole residual com-

Table 2. The total number of identified components contained in the h-RPG mixture

Components	Mol. wt.	bp(°C)	wt%	Mole fraction
CPD	66.1	41.0	0.07	0.0014
MCPD	81.0	72.0	0.02	0.0003
Toluene	92.1	110.6	0.01	0.0003
Ethylbenzene	106.2	136.2	0.13	0.0016
p-Xylene	106.2	136.4	0.18	0.0022
m-Xylene	106.2	139.1	0.70	0.0087
o-Xylene	106.2	142.0	1.47	0.0183
iso-Propylbenzene	120.2	152.4	0.60	0.0066
Styrene	104.2	145.2	2.80	0.0354
n-Propylbenzene	104.2	159.2	0.79	0.0100
m,p-Ethyltoluene	122.0	162.0	7.24	0.0782
1,3,5-Trimethylbenzene	120.2	164.7	2.24	0.0246
o-Ethyltoluene	120.2	165.2	2.01	0.0220
1,2,4-Trimethylbenzene	120.2	169.4	6.26	0.0686
α -Methylstyrene	118.2	165.6	1.29	0.0144
DCPD	102.0	166.6	1.46	0.0189
cis- β -Methylstyrene	118.2	167.5	0.92	0.0103
o-Vinyltoluene	118.2	169.8	4.11	0.0458
m-Vinyltoluene	118.2	171.6	8.63	0.0962
p-Vinyltoluene	118.2	172.8	4.08	0.0455
1,2,3-Trimethylbenzene	120.2	176.1	1.21	0.0133
m-Diethylbenzene	134.2	181.1	0.23	0.0023
m-n-Propyltoluene	136.0	182.0	0.56	0.0054
p-n-Propyltoluene	136.0	185.0	0.30	0.0029
Indane	18.2	176.5	1.11	0.0124
1,3-Dimethyl-5-ethylbenzene	134.2	183.6	1.01	0.0099
trans- β -Methylstyrene	118.2	179.0	2.25	0.0251
1,4-Dimethyl-2-ethylbenzene	134.2	186.9	0.17	0.0017
1,3-Dimethyl-4-ethylbenzene	134.2	188.2	0.37	0.0036
1,2-Dimethyl-4-ethylbenzene	134.2	189.5	0.49	0.0048
Methylindanes	133.0	197.5	0.35	0.0035
Indene	116.2	182.2	10.03	0.1138
m-Ethylstyrene	132.2	190.1	0.45	0.0045
p-Ethylstyrene	132.2	192.8	0.16	0.0016
2,4-Dimethylstyrene	132.2	195.0	0.23	0.0023
3,5-Dimethylstyrene	132.2	199.0	0.23	0.0023
1,2,3,4-Tetramethylbenzene	134.2	205.1	0.12	0.0018
3-Methylindene	130.2	206.0	0.27	0.0027
2-Methylindene	130.2	208.0	0.08	0.0008
Naphthalene	128.2	218.0	0.14	0.0014
Other C_{10} staurates	134.2	190.0	7.00	0.0687
C_{11} heavier	142.2	240.6	15.66	0.1451
Thermal polymerized resin	254.4	372.2	12.56	0.0651

ponents contained in the h-RPG are treated by a continuous fraction and it is modeled by an appropriate distribution function as shown in Fig. 3.

Table 3. Selected 6 pseudocomponents and their physical properties

Components	Mol. wt.	bp(K)	wt%	Mole fraction
m,p-Ethyltoluene	122.0	435.2	16.26	0.184170
1,2,4-Trimethylbenzene	120.2	442.5	11.02	0.126699
m-Vinyltoluene	118.2	444.8	21.15	0.247303
Indene	116.2	455.4	12.78	0.152028
C ₁₀ -C ₁₁	142.2	513.8	22.8	0.221577
H-resin	254.4	645.4	12.56	0.068223

CONTINUOUS THERMODYNAMIC PHASE EQUILIBRIUM CALCULATIONS

1. Distribution Function

For the continuous distribution functional treatment of the h-RPG as shown in Fig. 3, the remaining whole finite components in the h-RPG except the discretely assumed components such as the CPD, the MCPD and the TPR (Table 2) are not identified in detail but the fraction is characterized using the boiling point fractional index I , as a distribution variable. Instead of mole fractions, we now have a distribution function $F(I)$. This distribution function is normalized such that,

$$\int_I F(I) dI = 1.0 \quad (1)$$

over the proper range of I . When we model the h-RPG by the semicontinuous mixture, the continuous fraction is weighted with a mole fraction denoted η and each discrete component i is weighted with mole fractions x_i . Then for n discrete components with the continuous fraction, the normalization expressed by

Eq. (1) becomes,

$$\sum_i x_i + \eta \int_I F(I) dI = 1.0 \quad (1a)$$

where the distribution function $F(I)$ for the continuous fraction is described by a gamma distribution function since the continuous fraction follows qualitatively the correct feature of the function. Thus, the normalized distribution function is related to gamma function by,

$$F(I) = \frac{(I-\gamma)^{\beta-1}}{\beta^\beta \Gamma(\beta)} \exp\left(-\frac{(I-\gamma)}{\alpha}\right) \quad (2)$$

where Γ is gamma function given by,

$$\Gamma(\alpha) = \int_0^\infty I^{\alpha-1} e^{-I} dI \quad (3)$$

where α and β are adjustable parameters. The means is $\alpha\beta + \gamma$ and the variance is $\alpha\beta^2$, respectively. Shift parameter γ indicates the origin of $F(I)$; this parameter is the same for vapor and liquid phase.

2. Quadrature Method and Flash Calculation Procedure

Phase equilibrium calculations for the h-RPG are based on an isothermal vapor-liquid flash as schematically shown in Fig. 4. Temperature, pressure and feed compositions are specified. The compositions and relative amounts of the outlet streams are to be calculated. The feed and outlet streams are related through material balances. The two outlet streams are defined to be in thermodynamic equilibrium. Then, the essence of flash problem is to solve simultaneously a set of material balances which relate the feed stream to the outlet streams, and phase equilibria for two ef-

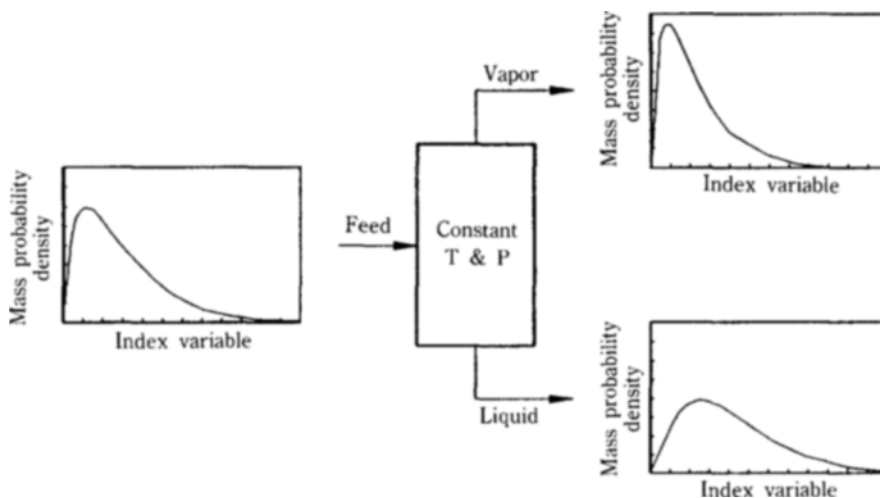


Fig. 4. Schematic representation of a flash calculation for a continuous mixture.

fluent streams for every component.

When we dealing with semicontinuous or continuous mixtures, however, the distribution functions for two equilibrated phases need to be related to one another. For example, if a gamma distribution describes the composition in one phase, that of the other phase is also described by a gamma function. When we use the distribution to the continuous fraction, relations can then be developed between parameters and for the vapor and for the liquid phase, so as to give a set of nonlinear equations. Solution of these equations gives the dew point and bubble point locus for the continuous fraction. If the composition of one phase is specified, the composition of the other can be found without approximation. However, when the same procedure is extended to flash case, the material balances must also be specified. Unfortunately, the material balances introduce a third distributions, namely, that of the feed. For the general case, there is no universal distribution function, applied to all three streams, for which phase equilibria and material balances can be satisfied for all values of index I . Therefore, the flash calculation for a continuous mixture can only intrinsically be solved approximately.

Currently two approximation methods-the method of moments and the quadrature method- are used to approximate the flash problems of a continuous mixtures. However, the method of moments provides only an approximate because it does not strictly satisfy all material balances. Thus, as an illustration, we present here only the quadrature method by following the framework discussed by Cotterman et al. [3, 4]. The quadrature method used an efficient numerical integration and it does not use an algebraic form for the distribution function but provides exact solutions to flash problem at representative values of the distribution variable. Especially when we use Gaussian integration formulae, the quadrature algorithm provides an efficient method of integrating a function by summing a finite number of weighted function evaluations at specified values of the integration variable called quadrature points. For each of these points, phase equilibria and material balances are satisfied exactly. For s quadrature points, the normalized distribution function of Eq. (1) can then be replaced by

$$\int_I F(I) dI = \sum_{p=1}^s W(I_p) f(I_p) \quad (4)$$

where $W(I_p)$ is the weighting factor and $f(I_p)$ is the integrand at the quadrature point, I_p . Then, for a semicontinuous mixture with n discrete components and m continuous fractions, the normalized condition for

the liquid stream is written

$$\sum_i^n x_i + \sum_k^m \eta_k^L \sum_p^s W(I_p) F_k^L(I_p) = 1.0 \quad (5)$$

Similar equations apply to feed and vapor streams. The quadrature point I_p and the $W_k(I_p)$ are the same in all streams. The phase equilibrium constraints must also be satisfied at each quadrature point p for each continuous fraction k

$$\mu_k^v(I_p) = \mu_k^l(I_p) \quad (6)$$

Equivalently, in terms of fugacity coefficients, ϕ_k

$$\eta_k^v F_k^v(I_p) \phi_k^v(I_p) = \eta_k^l F_k^l(I_p) \phi_k^l(I_p) \quad (7)$$

We define the fraction vaporized, ξ , as the ratio of moles of vapor to moles of feed. For every discrete component, i , the material balance is

$$z_i = \xi y_i + (1 - \xi) x_i \quad (8)$$

where z_i , y_i , and x_i are feed, vapor and liquid mole fractions, respectively. For the continuous fraction, the composition distribution of each stream is described by a collection of quadrature points, rather than by a gamma function. For every set of quadrature points, the material balance is

$$\eta^v F^v(I_p) = \xi \eta^v F^v(I_p) + (1 - \xi) \eta^l F^l(I_p) \quad (9)$$

Thus, the flash problem reduced to the simultaneous equation solving of a set of algebraic Eqs. (6) and (9).

The quadrature method is analogous to the well known pseudocomponent procedure. However, in the quadrature method, quadrature points and weighting factors are not arbitrary. They are determined from a class of orthogonal polynomials for s quadrature points, which integrate a polynomial of degree $2s-1$ exactly. As discussed later, the optimum number of quadrature points is chosen by increasing number until calculation results are constant within tolerable limits.

Flash calculation based on the quadrature method give values for the outlet streams' distribution functions, $F^v(I)$ and $F^l(I)$ at each quadrature point. Thus the quadrature method gives these functions only at discrete points, but it does so exactly.

3. Equation of State Consideration

In principle, any equation of state applicable to both the vapor and liquid phases may be used to obtain fugacity coefficient through the well-defined thermodynamic relation. However, the h-RPG mixture is mainly the C_9 fractions and we found through the preliminary test the well known Peng-Robinson equation of state (PR EOS) is relatively fit well the characteristics of the h-RPG. Thus we have chosen the PR EOS

among the popular cubics such as Redlich-Kwong-Soave and Patel-Teja EOSs [6].

The PR EOS is given by

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+b(V-b)} \quad (10)$$

where a and b for a semicontinuous mixture with n discrete components and m continuous fraction over quadrature points are given by

$$a = \sum_i^n \sum_j^n x_i x_j a(i, j) + 2 \sum_l^m \sum_k^m x_l \eta_k \sum_p^s W_k(I_p) F_k(I_p) a(i, I_p) + \sum_k^m \sum_l^m \eta_k \eta_l \sum_p^s \sum_q^s W_k(I_p) F_k(I_p) W_l(I_q) F_l(I_q) a(I_p, I_q) \quad (11)$$

$$b = \sum_i^n x_i b(i) + \sum_k^m \eta_k \sum_p^s W_k(I_p) F_k(I_p) b(I_p) \quad (12)$$

$$a(I) = a_c(I) \alpha(I) \quad (13)$$

$$a_c(I) = 0.457235 \frac{[RT_c(I)]^2}{P_c(I)} \quad (14)$$

$$\alpha^{0.5}(I) = 1 + [0.37646 + 1.542260\omega(I) - 0.26992\omega^2(I)] \times [1 - T_r^{0.5}(I)] \quad (15)$$

$$b(I) = 0.77796 \frac{RT_c(I)}{P_c(I)} \quad (16)$$

The cross coefficient for a between discrete and continuous fractions, I_p , and I_q , and i, j , respectively are given by the geometric mean with the binary interaction parameter k by

$$a(i, j) = a^{0.5}(i, i)a^{0.5}(j, j)(1 - k_{ij}) \quad (17a)$$

$$a(i, I) = a^{0.5}(i, i)a^{0.5}(I, I)(1 - k_{iI}) \quad (17b)$$

$$a(I_p, I_q) = a^{0.5}(I_p, I_p)a^{0.5}(I_q, I_q)(1 - k_{I_p I_q}) \quad (17c)$$

However the binary interaction parameters, k_{ij} , k_{iI} , $k_{I_p I_q}$ are assume to be 0, since the h-RPG is mainly aromatic homologous C_9 fraction and safely can avoid any significant error in the flash calculation with this simplification. An expression for the fugacity coefficient derived using PR EOS with respect to the s quadrature points is given by

$$RT \ln \phi_k(I_p) = RT \ln \frac{V}{V-b} + (z-1) \frac{b(I_p)}{b} + \frac{a}{2^{1.5} b^2} \ln \left(\frac{V + (2^{0.5} + 1)b}{V - (2^{0.5} + 1)b} \right) - \frac{2}{2^{1.5} b} \left\{ \sum_i^n x_i a(I_p) + \sum_i^m \eta_i \sum_q^s \omega_i(I_p) F_i(I_q) a(I_p, I_q) \right\} \times \ln \left\{ \frac{V + (2^{0.5} + 1)b}{V - (2^{0.5} + 1)b} \right\} - RT \ln Z \quad (18)$$

where Z denotes compressibility factor. Here the parameter $b(I_p)$ and $a(I_p, I_p)$ are found from PR EOS information at each quadrature point. The cross coefficients $a(I_p, I_q)$ are found from the geometric mean of $a(I_p, I_p)$ and $a(I_q, I_q)$. The binary interaction parameter k_{I_p, I_q} assumed as 0. Other pure component parameters such as critical point data at each component are used the correlations reported in the data book [9, 10] and other literature [11]. Eq. (11), (12), and (13) are written for each equilibrium phase to relate $F_k^V(I_p)$ to $F_k^L(I_p)$. Fugacity coefficient expressions for discrete components are derived by the analogy to Eq. (11).

RESULTS AND DISCUSSION

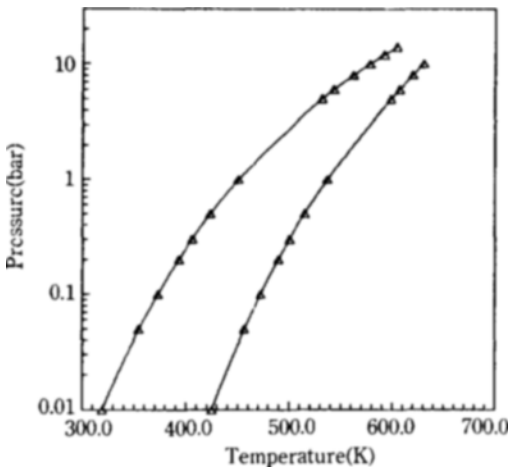
Phase equilibrium calculations are carried out for the following 4 cases;

- Case I. Rigorous pseudocomponent method by set the h-RPG as the discrete mixture of 43 finite components,
- Case II. Pseudocomponent method by set the h-RPG as the mixture of 6 representative components,
- Case III. Semicontinuous methods by set the h-RPG as the mixture of 3 discrete components (CPD, MCPD, and TPR) and continuous fraction,
- Case IV. Semicontinuous methods by set the h-RPG as the mixture of 2 discrete (CPD, MCPD) components and continuous fraction.

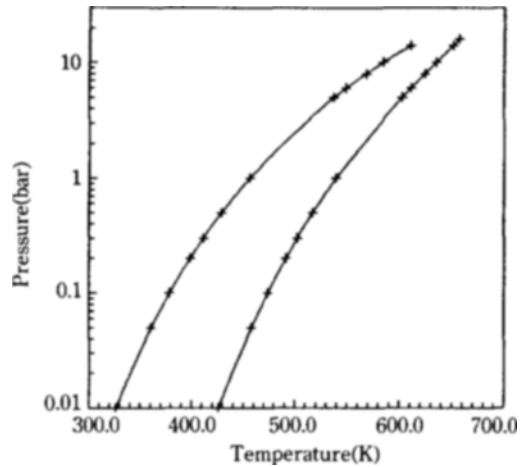
The calculation results for above four cases are compared together.

1. Bubble and Dew Point Calculations

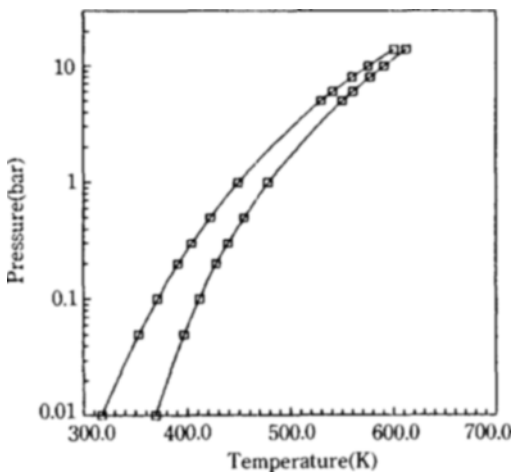
The calculated results for cases I to IV for bubble and dew points for a feed h-RPG mixture are summarized in Figs. 5, 6 and 7. The smooth solid lines in these figures are simply obtained by the method of cubic spline interpolation with respect to the calculated representative data points. The results for each case are compared separately in Fig. 5 and they compared together in Fig. 6. The results for low pressure region is shown in detail in Fig. 7. As one might expect, the calculated bubble and dew point locus for case I and II are reasonable agree well each other within the point of process design engineering view. However, when we treat the h-RPG as the combination of a semicontinuous mixture with a number of discrete components, the results strongly depend on the way of choosing discrete components. As we discussed in the earlier section, we simply assumed the h-RPG consists



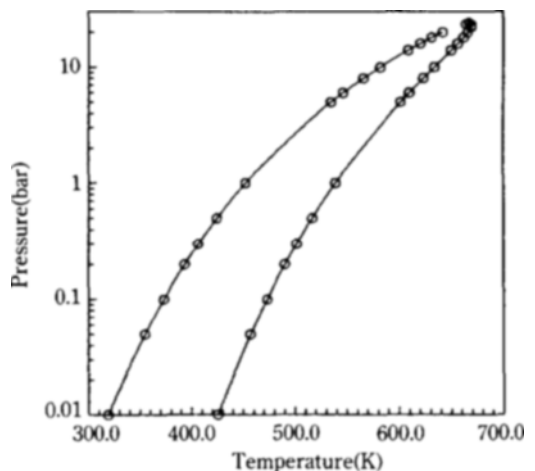
(a) 43 components



(b) 6 pseudo-components



(c) 2-discrete components and continuous fraction



(d) 3-discrete components and 1 continuous fraction

Fig. 5. Calculated bubble and dew point locus for h-RPG.

of 43 finite components. However, the TPR is not truly a single component. Practically it is very difficult to identify exactly the actual constituents of the TPR by the gas chromatographic analysis. We arbitrarily in a sense treated the TPR as a pseudocomponent as the cases of CPD and MCPD. Furthermore, the h-RPG contained 12.56% of the TPR. Thus, depend on whether the TPR is treated as a discrete component(case III) or not(case IV), the calculated results for the case III and IV are significantly differ from each other.

While the result for the case III agree well with the case I and II, the case IV shows a significant error with respect to the cases of I, II, and III. Also, we observed that there are significant difficulty in calculating the bubble and dew points in the neighborhood

of the mixture pseudocomponent point for the cases I and II as shown in Fig. 5(a) and (b). However, it was possible to calculate the bubble and dew points even in the near-pseudocritical point of the mixture when we adapt the continuous thermodynamic framework to the mixture as shown in Fig. 5(c) and (d). Also, in the cases III and IV, we observed that the optimum number of the quadrature points are 3, 4 or 5 as shown in Table 4. Thus, we constructed the Figs. 5 to 7 based on the results with 5 quadrature points. As one can see in Table 4, the quadrature point 5 can guarantee the reasonable accuracy in approximating the continuous fraction while keeping the economic CPU time.

2. Flash Calculation

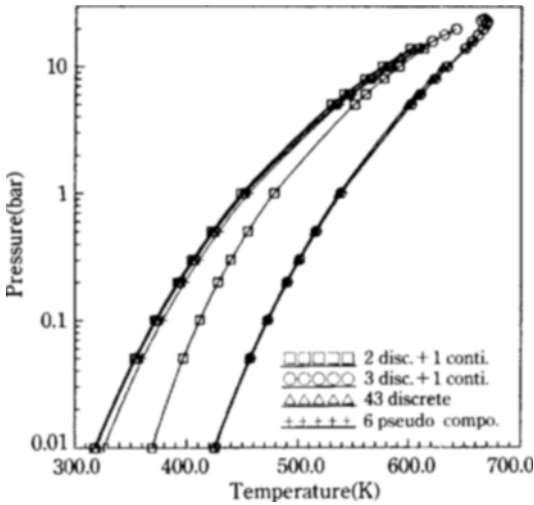


Fig. 6. Comparison of calculated bubble and dew point locus for 4 cases of h-RPG.

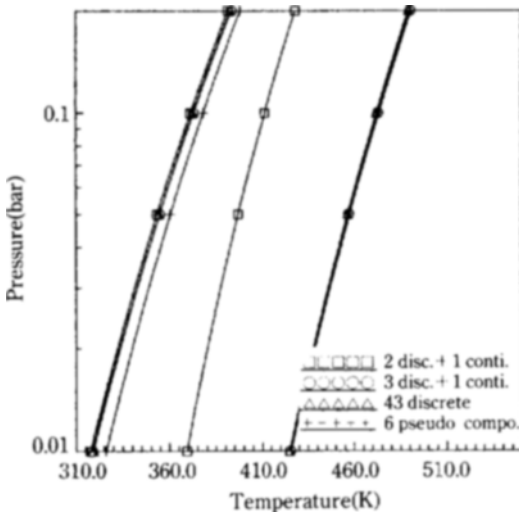


Fig. 7. Detailed comparison of the calculated bubble and dew point locus for 4 cases of h-RPG in the low temperature region.

Based on the information obtained in the previous section, we performed isothermal flash calculation by solving simultaneously the material balance equations and the phase equilibrium relations where we chose the flash conditions by 460 and 470 K at 1.013 bar, respectively. These flash conditions are selected arbitrarily. In cases III and IV, we found the optimum number of the quadrature points by simply increasing the number from 3 to 8. These results are also summarized in Table 6. If we compare the accuracy and

Table 4. CPU and accuracies for the calculations by the methods of the quadrature and pseudocomponent (IBM PC/286)

Characterization	Bubble point(K)	Dew point(K)	Flash calculation	
			ξ	T = 470 K CPU(sec)
43 finite components	450.9	537.5	0.691	20.54
6 pseudocomponents	456.2	539.9	0.562	1.76
3 point quadrature	452.4	538.9	0.570	1.43
4 point quadrature	453.6	539.0	0.588	1.56
5 point quadrature	452.8	539.1	0.573	1.69
6 point quadrature	452.7	539.1	0.574	1.82
7 point quadrature	452.7	539.1	0.574	1.95
8 point quadrature	452.7	539.1	0.574	2.03

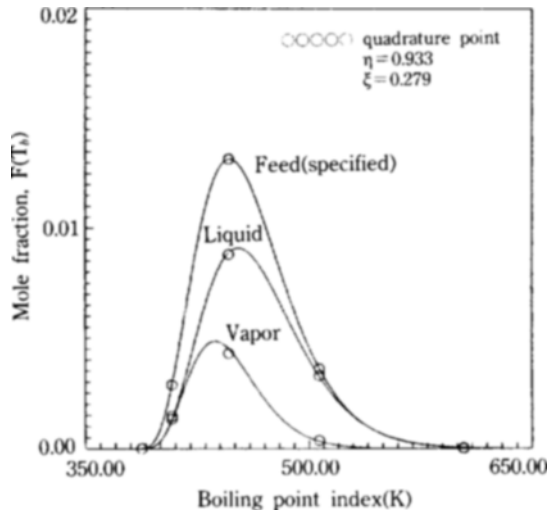


Fig. 8. Flash calculated results at 460 K and 1.013 bar for the semicontinuous h-RPG using 5 quadrature points.

CPU time for case II and III in conjunction with the reference case I, the case III in which we treated the feed h-RPG as a semicontinuous mixture with 3 discrete components show better result with less CPU time than the conventional pseudocomponent method (case II) within the tolerable error limit. One of the flash calculation results at 460 K and 1.013 bar for the feed h-RPG is shown in Fig. 8 where the result is based on the quadrature point 5 and the results for the discrete component such as CPD, MCPD and the TPR are omitted in Fig. 8. We concluded that the continuous thermodynamic calculation for the case III with 5 quadrature points consistently better than the case of 6 pseudocomponent method.

CONCLUSION

We illustrated the usefulness of the continuous thermodynamic framework when we need to perform rigorously a fluid phase equilibrium and the related process calculation for the mixtures such as the h-RPG which contain far too many components for standard chemical analysis.

Besides, the results obtained in the present study for industrially important heavy raw pyrolysis gasoline might be directly extended toward a practical separation process calculation purpose to produce a favorable raw materials in petroleum resin synthetic industry.

ACKNOWLEDGEMENT

The authors are grateful to Sogang University for the partial financial support. They also acknowledge the Owoon Foundation for the financial support.

NOMENCLATURE

a	: constant in Peng-Robinson equation of state [Pa m ⁶ /mol ²]
b	: constant in Peng-Robinson equation of state [m ³ /mol]
k	: binary interaction parameter
F(I)	: distribution function
I	: continuous distribution variable
n	: number of discrete component
P	: pressure [bar]
R	: gas constant [m ³ bar/mol °K]
T	: temperature [°K]
V	: molar volume [m ³ /mol]
W	: weighting factor in the quadrature formulae
x, y, z	: mole fraction for liquid, vapor, and feed, respectively

Greek Letters

α, β, γ	: parameters in gamma distribution function
Γ	: gamma distribution function

μ	: chemical potential
η	: mole fraction for the continuous mixture
ϕ	: fugacity coefficient
ξ	: fraction of feed vaporized
ω	: escentric factor

Superscripts

F	: feed stream
L	: liquid stream
V	: vapor stream

Subscripts

i, j	: discrete components
k, l	: continuous fractions
p, q, m, s	: quadrature points

REFERENCES

1. Kamide, K.: Batch Fractionation, in Fractionation of Synthetic Polymers, edited by Tung, L. H., Marcel Dekker Inc., Ch. 2, p.103 (1977).
2. Hayashi, H.: *Org. Syn. Chem.*, **36**(6), 533 (1978).
3. Cotterman, R. L., Bender, R. and Prausnitz, J. M.: *Ind. Eng. Chem. Process Des. Dev.*, **24**, 194 (1985).
4. Cotterman, R. L. and Prausnitz, J. M.: *Ind. Eng. Chem. Process Des. Dev.*, **24**, 433 (1985).
5. Ratzsch, M. T. and Kehlen, H.: *Fluid Phase Equil.*, **14**, 225 (1983).
6. Willman, B. T. and Teja, A. S.: *AIChE J.*, **32**, 2067 (1986).
7. Kim, S. W., Rho, H. K. and Kim, H. S.: *Hwahak Konghak*, **29**, 654 (1991).
8. American Petroleum Institute Technical Data Book -Petroleum Refining, Washington, USA (1980).
9. Fussel, D. D. and Yanosik, J. L.: *Soc. Pet. Eng. J.*, **18**, 174 (1978).
10. Reid, R. C., Prausnitz, J. M. and Poling, B. E.: *The Properties of Gases and Liquids*, 4th Eds., McGraw-Hill, New York, USA (1988).
11. Twu, C. H.: *Fluid Phase Equil.*, **16**, 137 (1984).