Cubic and non-cubic 상태방정식의 LNG 물성 예측 비교

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LNG thermodynamic properties prediction by use of non-cubic & cubic equation of state

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1. 서론

본 연구에서는 Hydrocarbon Systems의 물성 예측에 cubic형태의 Peng Robin-son 상태방정식(PREOS)과 Non-cubic형태의 Benedict-Webb-Rubin-Starling (BWRS)상태 방정식을 사용하여 그 결과를 비교하였다.

2. 이론

1) PR-EOS

$$P=\frac{RT}{V-b}-\frac{\theta_{PR}}{V^2+2bV-b^2}$$

$$\theta_{PR}=a''[1+(0.37464+1.54226\omega-0.26992\omega^2)(1-T_r^{1/2})]^2$$

$$a''=\frac{0.45724R^2T_c^2}{P_c}, \qquad b=\frac{0.07780R^2T_c^2}{P_c}$$

2) BWRS-EOS

$$P = \rho RT + (B_oRT - A_o - \frac{C_o}{T^2} + \frac{D_o}{T^3} - \frac{E_o}{T^4})\rho^2 + (bRT - a - \frac{d}{T})\rho^3 + \alpha(a + \frac{d}{T})\rho^6 + \frac{c\rho^3}{T^2}(1 + \gamma\rho^2)\exp(-\gamma\rho^2)$$

11개의 순수물질 parameter는 다음 식으로 계산된다. (Han&Starling Correlation)

$$\rho_{ci} B_{oi} = A_1 + B_1 \omega_i \qquad (\rho_{ci} A_{oi})/(R T_{ci}) = A_2 + B_2 \omega_i$$

$$(\rho_{ci}^2 C_{oi})/(R T_{ci}^3) = A_3 + B_3 \omega_i \qquad \rho_{ci}^2 \gamma_i = A_4 + B_4 \omega_i$$

$$\rho_{ci}^2 b_i = A_5 + B_5 \omega_i \qquad (\rho_{ci}^2 a_i)/(R T_{ci}^3) = A_6 + B_6 \omega_i$$

$$\rho_{ci}^3 \alpha_i = A_7 + B_7 \omega_i \qquad (\rho_{ci}^2 c_i)/(R T_{ci}^3) = A_8 + B_8 \omega_i$$

$$(\rho_{ci} D_{oi})/(R T_{ci}^4) = A_9 + B_9 \omega_i \qquad (\rho_{ci}^2 d_i)/(R T_{ci}^2) = A_{10} + B_{10} \omega_i$$

$$(\rho_{ci} E_{oi})/(R T_{ci}^5) = A_{11} + B_{11} \omega_i \exp(-3.8 \omega_i)$$

The Bishinoi-Robinson Mixing Rules(BR MR)

$$B_{oij} = \sum_{i=1}^{n} x_i B_{oi}$$

$$A_o = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j A_{oi}^{\frac{1}{2}} A_{oj}^{\frac{1}{2}} (1-k_{ij})$$

$$C_o = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j C_{oi}^{\frac{1}{2}} C_{oj}^{\frac{1}{2}} (1-k_{ij})^3 \qquad \gamma = \left[\sum_{i=1}^{n} x_i \gamma_i^{\frac{1}{2}} \right]^2$$

$$b = \left[\sum_{i=1}^{n} x_i b_i^{\frac{1}{3}} \right]^3 \qquad a = \left[\sum_{i=1}^{n} x_i a_i^{\frac{1}{3}} \right]^3$$

$$\alpha = \left[\sum_{i=1}^{n} x_i \alpha_i^{\frac{1}{3}} \right]^3 \qquad c = \left[\sum_{i=1}^{n} x_i c_i^{\frac{1}{3}} \right]^3$$

$$D_o = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j D_{oi}^{\frac{1}{2}} D_{oj}^{\frac{1}{2}} (1-k_{ij})^4 \qquad d = \left[\sum_{i=1}^{n} x_i d_i^{\frac{1}{3}} \right]^3$$

$$E_o = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j E_{oi}^{\frac{1}{2}} E_{oj}^{\frac{1}{2}} (1-k_{ij})^4$$

Modified van der Waals one fluid Mixing Rules(CST MR)

$$\sigma_x^3 = \sum_{\alpha} \sum_{\beta} x_\alpha x_\beta \sigma_{\alpha\beta}^3$$

$$\varepsilon_x \sigma_x^3 = \sum_{\alpha} \sum_{\beta} x_\alpha x_\beta \varepsilon_{\alpha\beta} \sigma_{\alpha\beta}^3$$

$$\gamma_x \varepsilon_x^2 \sigma_x^3 = \sum_{\alpha} \sum_{\beta} x_\alpha x_\beta \gamma_{\alpha\beta} \varepsilon_{\alpha\beta}^2 \sigma_{\alpha\beta}^3$$

$$\sigma_{\alpha\beta} = \xi_{\alpha\beta} \sqrt{\sigma_{\alpha\alpha} \sigma_{\beta\beta}}$$

$$\varepsilon_{\alpha\beta} = \zeta_{\alpha\beta} \sqrt{\varepsilon_{\alpha\alpha} \varepsilon_{\beta\beta}}$$

$$\gamma_{\alpha\beta} = \frac{1}{2}(\gamma_{\alpha\alpha} + \gamma_{\beta\beta})$$

BWRS 상태방정식에 두가지 다른 Mixing Rules를 사용하여 밀도와 액상 조성에 대한 예측성을 비교하여 Table 1에 나타내었다.

Table 1. Comparison of prediction for hydrocarbon systems.
systems.

Binary Systems	EOS	A.A.D.(%) Density	No. of Data points	A.A.D.(%) VLE (x_i)	No. of Data points
$CH_4/n-C_4H_{10}$	CST MR	1.6	6	9.2	14
	BR MR	4.0	6	11.8	14
$C_2H_8/n-C_5H_{12}$	CST MR	2.4	12	8.49	12
	BR MR	2.5	12	8.51	12
$C_3H_{12}/n-C_6H_{14}$	CST MR			16.3	10
	BR MR			12.7	10
$C_4H_{15}/n-C_7H_{16}$	CST MR	3.4	12	23.5	10
	BR MR	2.6	12	31.5	10

Non-cubic 형태의 BWRS 상태방정식으로 hydrocarbon 이성분계의 물성을 예측한 결과, cubic식인 PREOS에 비해 전반적으로 예측성이 뛰어남을 알 수 있었다. 다성분계에 대한 연구가 더 진행되어야 할 것이다.

3. 참 고 문 헌

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