Equation of State Modeling of Phase Equilibrium in the Low-Density Polyethylene Process

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LDPE Process

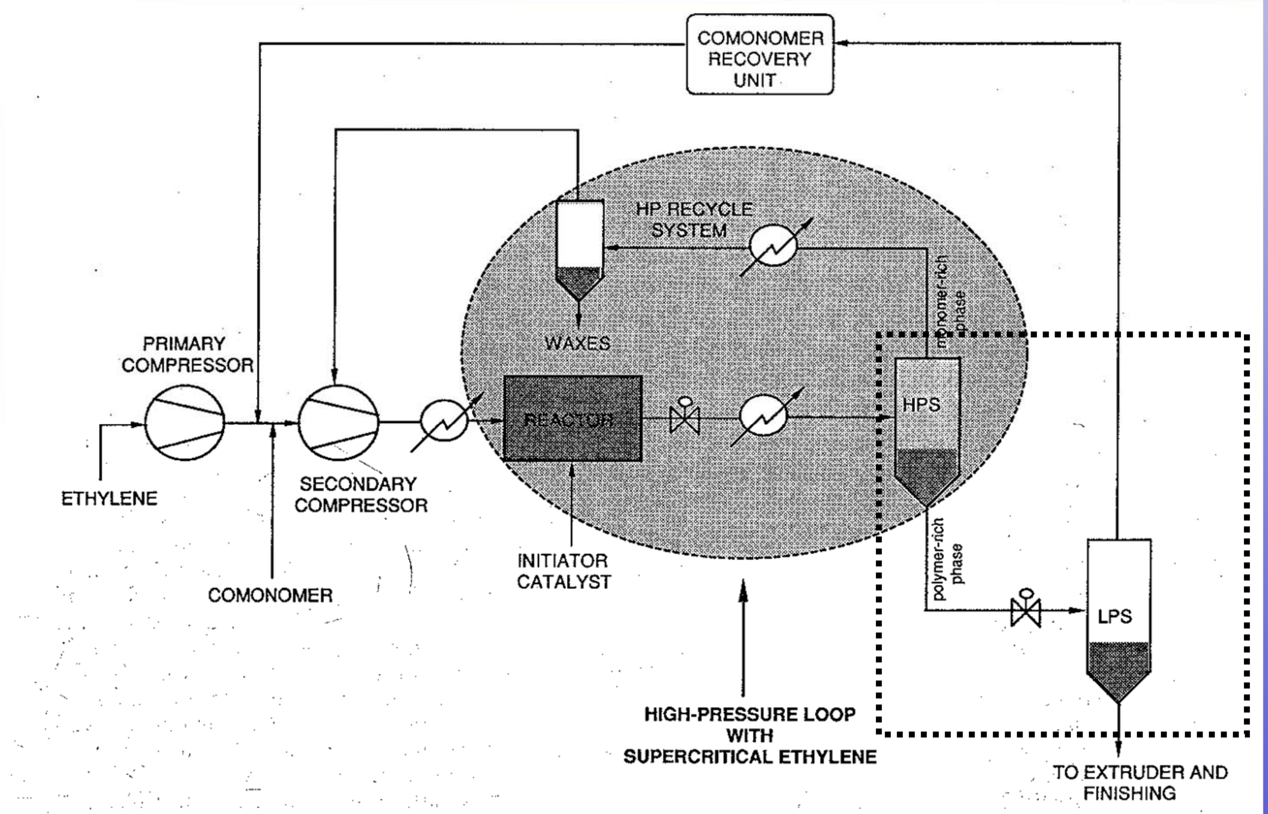


Figure 1. Simplified flow diagram of the HPPE process.

Bernard et al., ”Phase Equilibrium in High-Pressure Polyethylene technology”, *I&EC*, **1995**, 34, 1501-1516

Modeling by Equation of State

- Characteristics of LDPE process
  - Highly non-ideal at high pressure
  - Difference in size between polymer and solvent
  - Broad molecular weight distribution
  - Existence of variable multi-phase

- Advantage on using equation of state
  - Application to the region between low pressure to supercritical condition
  - Unified method to predict the behavior of multi-phase equilibria
  - Ability of describing volumetric, calorimetric and phase equilibrium properties at the same time

Sanchez-Lacombe Lattice Model (SL model)

- Pressure

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}\left[\ln(1 - \tilde{\rho} + \left(1 - \frac{1}{r}\right)\tilde{\rho}\right] = 0$$

$$\tilde{T} = \frac{T}{T^*} \quad \tilde{P} = \frac{P}{P^*} \quad \tilde{\rho} = \frac{\rho}{\rho^*} \qquad \text{with} \quad T^* = \frac{\varepsilon^*}{k} \quad P^* = \frac{\varepsilon^*}{v^*} \quad \rho^* = \frac{M}{rv^*}$$

- Parameters and mixing rule

$$v^*_{mix} = \sum_i \sum_j \phi_i \phi_j v^*_{ij} \qquad \varepsilon^*_{mix} = \frac{1}{v^*_{mix}} \sum_i \sum_j \phi_i \phi_j \varepsilon^*_{ij} v^*_{ij} \qquad \frac{1}{r_{mix}} = \sum_i \frac{\phi_i}{r_i}$$

$$\phi_i = \left(\frac{w_i}{\rho^*_i v^*_i}\right) \Big/ \sum_j \frac{w_j}{\rho^*_j v^*_j} \qquad v^*_{ij} = \left(v^*_{ii} + v^*_{jj}\right)\left(1 - l_{ij}\right)/2 \qquad \varepsilon^*_{ij} = \sqrt{\varepsilon^*_{ii}\varepsilon^*_{jj}}\left(1 - k_{ij}\right)$$

Statistical Associating Fluid Theory (SAFT)

- Compressibility factor

$$Z = \frac{Pv}{RT} = 1 + Z_{hs} + Z_{disp} + Z_{chain} + Z_{assoc}$$

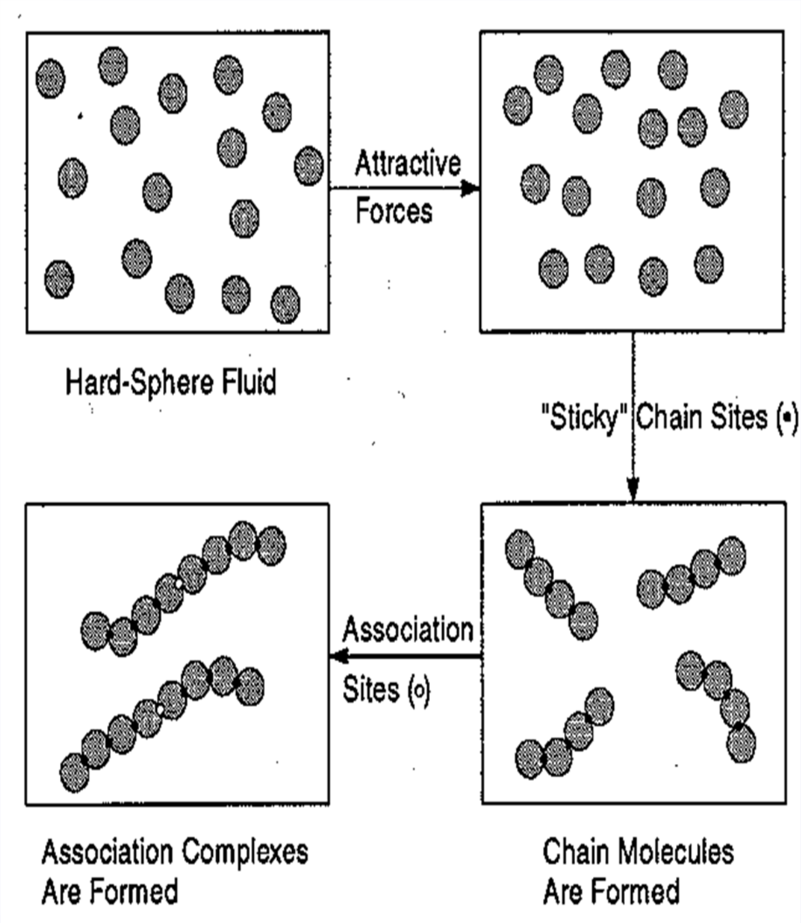
$$Z_{hs} = \frac{6}{\pi N_A \rho}\left[\frac{\xi_0\xi_3}{1-\xi_3} + \frac{3\xi_1\xi_2}{(1-\xi_3)^2} + \frac{(3-\xi_3)\xi_2^3}{(1-\xi_3)^3}\right]$$

$$Z_{disp} = r\sum_n\sum_m mD_{nm}(u/kT)^n\left(\xi_3/\xi_{3cp}\right)^m$$

$$Z_{chain} = \sum_i x_i(1-r_i)L(d_i)$$

$$Z_{assoc} = \rho\sum x_i\left[\sum\left(1/X^{S_i} - 1/2\right)\left(\partial X^{S_i}/\partial\rho\right)\right]$$

$$X^{S_i} = \left(1 + N_A\sum_j\sum_{Y_j} x_j\rho X^{Y_j}W_{ij}\right)^{-1}$$



Statistical Associating Fluid Theory (SAFT)

- Parameters

$$\eta = 0.74048\rho m v^0 \qquad v^0 = v^{00}\left[1 - C\exp\frac{-3u^0}{kT}\right]^3 \qquad u = u^0\left[1 + \frac{e}{kT}\right]$$

- Mixing rule

$$v_{ij}^0 = \left[\frac{1}{2}\left((v_i^0)^{1/3} + (v_j^0)^{1/3}\right)\right]^3 \qquad u_{ij} = (1 - k_{ij})\left(u_{ii}u_{jj}\right)^{1/2} \qquad m_{ij} = \frac{(m_i + m_j)}{2}(1 - l_{ij})$$

$$\frac{u}{kT} = \frac{\sum_i\sum_j x_i x_j m_i m_j \frac{u_{ij}}{kT}(v^0)_{ij}}{\sum_i\sum_j x_i x_j m_i m_j (v^0)_{ij}} \qquad m = \sum_i\sum_j x_i x_j m_{ij}$$

Polymer-SRK Equation of State

- Pressure

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)} \quad \text{with} \quad b = 0.08664\frac{RT_c}{P_c} \quad \text{and} \quad a = 0.42748\frac{R^2T_c^2}{P_c}\alpha$$

$$\alpha = [1 + C_1(1 - T_R^{0.5}) + C_2(1 - T_R^{0.5})^2 + C_3(1 - T_R^{0.5})^3]^2$$

  - For polymer

$$\frac{T_c^P - 1300}{T_c^m - 1300} = \frac{1}{D_P^{0.25}} \quad T \text{ in Kelvin} \quad \frac{P_c^P - 5}{P_c^m - 5} = \frac{1}{D_P} \quad P \text{ in bar and} \quad D_P = \frac{M_n}{M_{monomer}}$$

- Parameters and mixing rule

$$b = \sum_i x_i b_i$$

$$\frac{a}{bRT} = \sum_i x_i \frac{a_i}{RTb_i} - 1.546\left(\frac{G^{ex}}{RT} + \sum_i x_i \ln\frac{b}{b_i}\right)$$

Determination of Pure Component Parameters

- Ethylene
  - Using the vapor pressure and saturated liquid and vapor density
  - All models should represent the behavior of supercritical region.

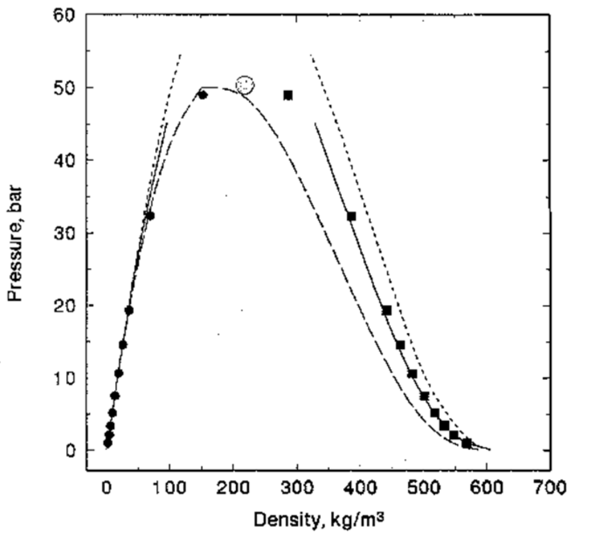


Figure 1. Properties of saturated ethylene from various EOS models. The points represent data from Beaton and Hewitt.[12] The solid lines are estimations from the SAFT model, the long-dashed lines are estimations from the polymer-SRK model, and the short-dashed lines are estimations from the SL model.

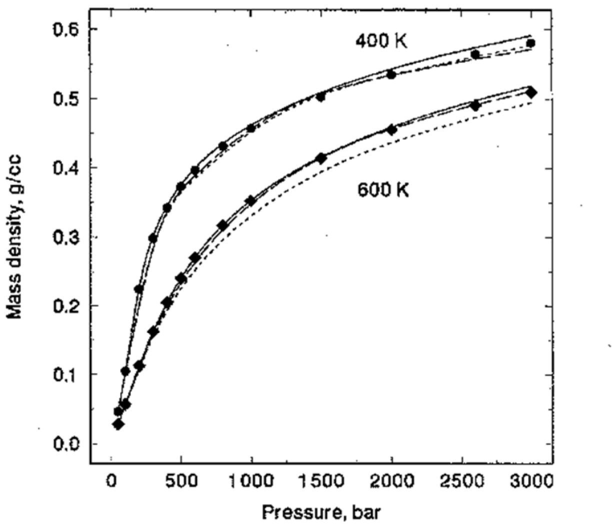


Figure 2. Density of supercritical ethylene at 400 and 600 K from various EOS models. The points represent data from Sychev et al.[13] The solid lines are estimations from the SAFT model, the long-dashed lines are estimations from the polymer-SRK model, and the short-dashed lines are estimations from the SL model.

Determination of Pure Component Parameters

- Polyethylene
  - All models should represent properties for a different number-average molecular weight

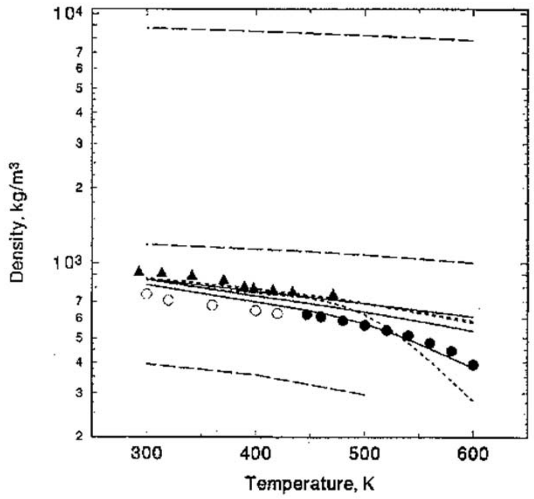


Figure 4. Density estimations for polyethylene chains containing 500, 50, and 5 ethylene repeat units as a function of temperature at 1 bar pressure from various EOS models. The triangular points represent data for polyethylene from Danner and High;[8] the dots represent data for *n*-decane from Beaton and Hewitt[12] (●) and Perry and Green[29] (○). The solid lines are estimations from the SAFT model, the long-dashed lines are estimations from the polymer-SRK model, and the short-dashed lines are estimations from the SL model.

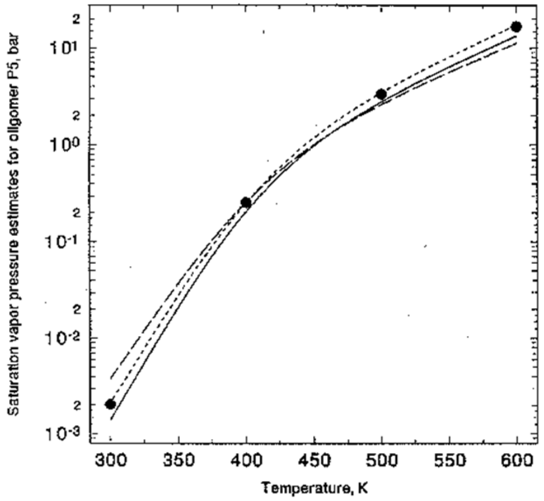


Figure 5. Saturation vapor pressure estimations for a polyethylene chain with five ethylene repeat units as a function of temperature from various EOS models. The solid line is estimations from the SAFT model, the long-dashed line is estimations from the polymer-SRK model, and the short-dashed line is estimations from the SL model. The points represent experimental vapor pressure data for *n*-decane from Beaton and Hewitt.[12]

Determination of Pure Component Parameters

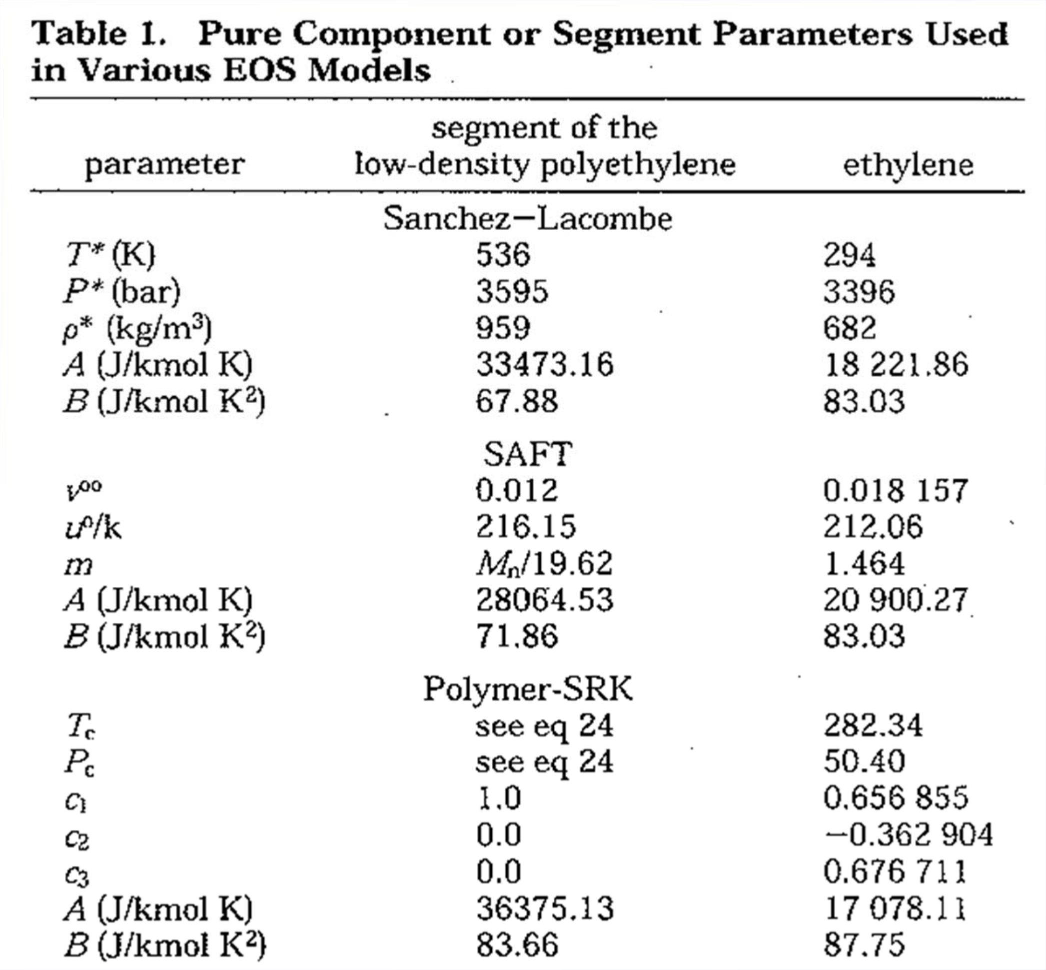


Table 1. Pure Component or Segment Parameters Used in Various EOS Models

parameter	segment of the low-density polyethylene	ethylene
	Sanchez−Lacombe	
T^* (K)	536	294
P^* (bar)	3595	3396
ρ^* (kg/m^3)	959	682
A (J/kmol K)	33473.16	18 221.86
B (J/kmol K^2)	67.88	83.03
	SAFT	
v^{oo}	0.012	0.018 157
u^o/k	216.15	212.06
m	$M_n/19.62$	1.464
A (J/kmol K)	28064.53	20 900.27
B (J/kmol K^2)	71.86	83.03
	Polymer-SRK	
T_c	see eq 24	282.34
P_c	see eq 24	50.40
c_1	1.0	0.656 855
c_2	0.0	−0.362 904
c_3	0.0	0.676 711
A (J/kmol K)	36375.13	17 078.11
B (J/kmol K^2)	83.66	87.75

Correlation of Binary VLE of ethylene-LDPE mixture

- SAFT model
  - The difference between using two binary parameters versus one binary parameter is not very noticeable.

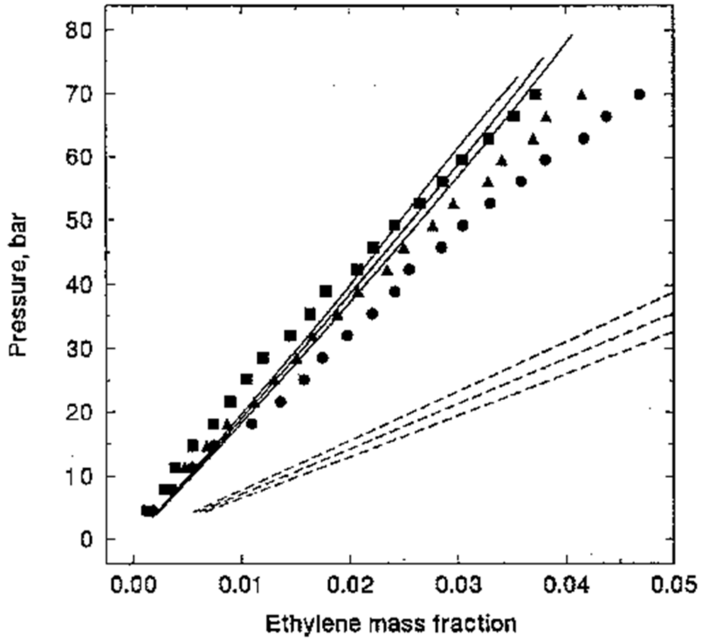
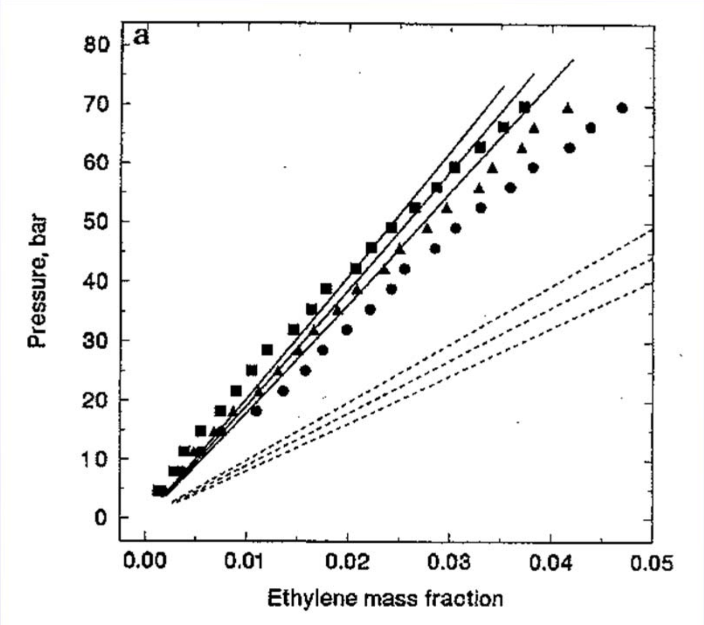


Figure 7. Vapor−liquid equilibrium between polyethylene (M_n = 31 700, M_w = 248 700) and ethylene at 399 K (●), 413 K (▲), and 428 K (■) from the SAFT model. The points represent data from the compilation of Hao et al.[15] The solid lines are the results of correlation with $\xi_{ij} = 0.1479$. The two-parameter correlation of the data results in parameters $\xi_{ij} = 0.1417$ and $\zeta_{ij} = 0.0013$; these results are not shown for brevity as they are very similar to the one-parameter correlation. The dashed lines are predictions obtained from the SAFT model with all binary parameters set to zero.

Correlation of Binary VLE of ethylene-LDPE mixture

- SL model
  - For using two binary parametes the model is capable of representing the high-pressure region better.



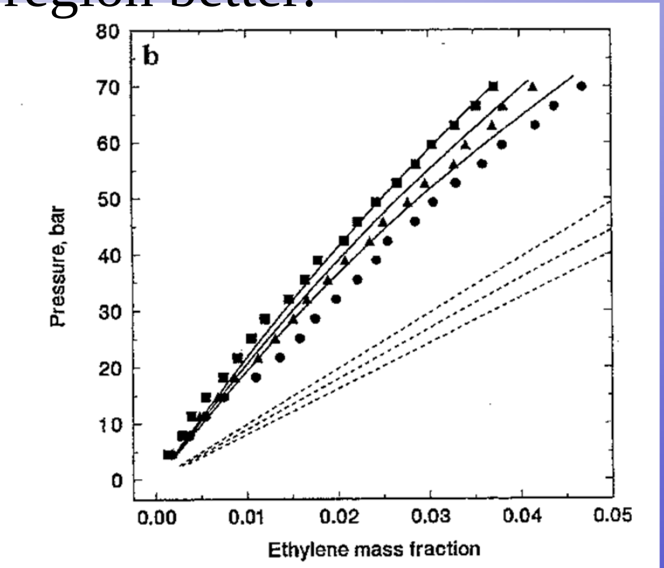


Figure 8. Vapor–liquid equilibrium between polyethylene (M_n = 31 700, M_w = 248 700) and ethylene at 399 K (●), 413 K (▲), and 428 K (■) from the SL model. The points are data from the compilation of Hao et al.;[15] the solid lines are the results of correlation with k_{ij} = 0.1060 (a) and with k_{ij} = −0.0093, l_{ij} = −0.4310 (b). The dashed lines are predictions obtained from the SL model with all binary parameters set to zero.

Correlation of Binary VLE of ethylene-LDPE mixture

- Polymer –SRK model
  - Using one binary parameter the model represents the VLE behavior quite accurately

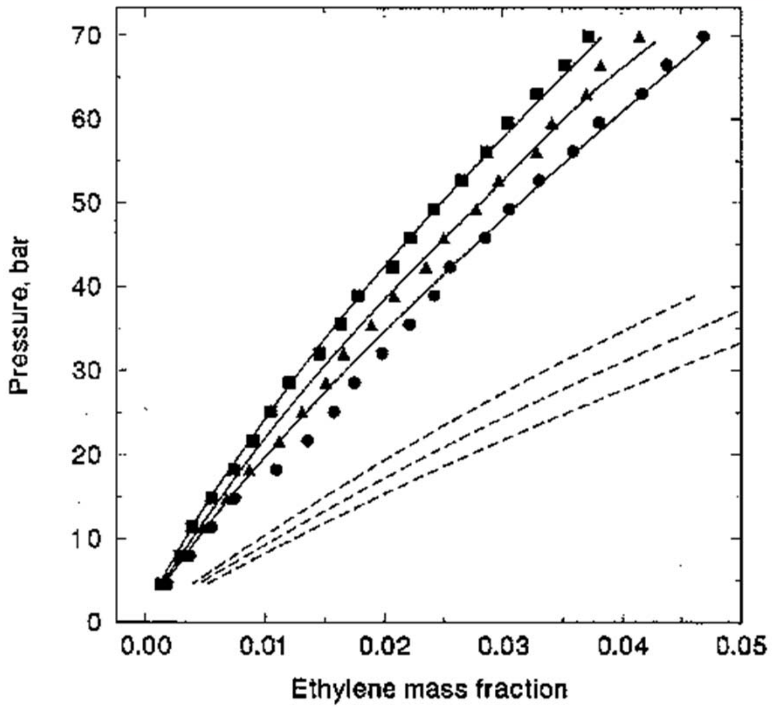


Figure 9. Vapor–liquid equilibrium between polyethylene (M_n = 31 700, M_w = 248 700) and ethylene at 399 K (●), 413 K (▲), and 428 K (■) from the polymer-SRK model. The points are data from the compilation of Hao et al.;[15] the solid lines are the results of correlation with χ = 1.05. The dashed lines are predictions obtained from the SAFT model with $\chi = 0$.

Simulation of Flash Operations in the LDPE process

- The estimation of the amount of monomer left in the final product
- Polymer residues in vapor phase => Flugging in recycle

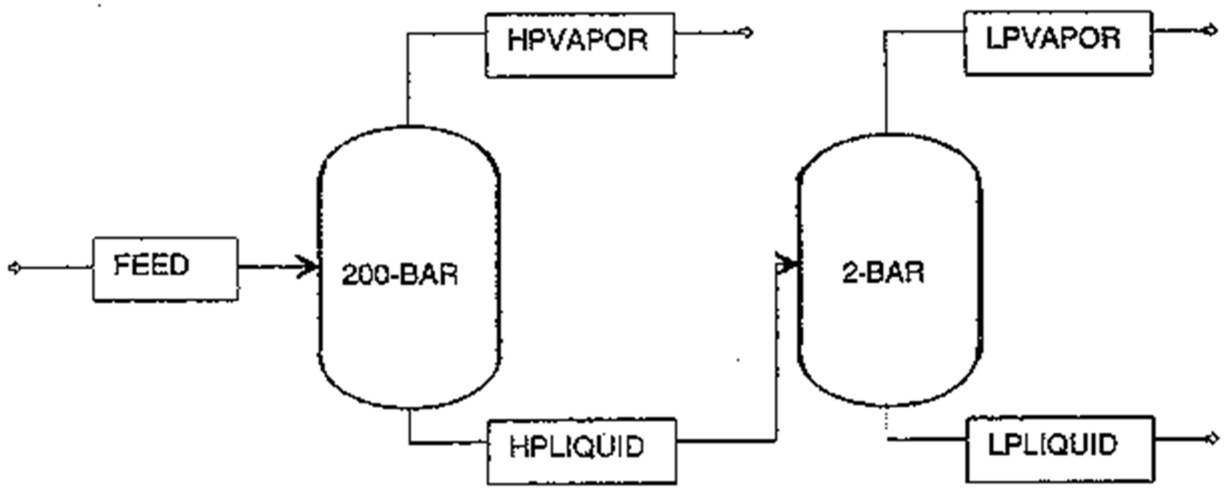


Figure 10. Schematic diagram of simulation flow sheet.

Simulation results

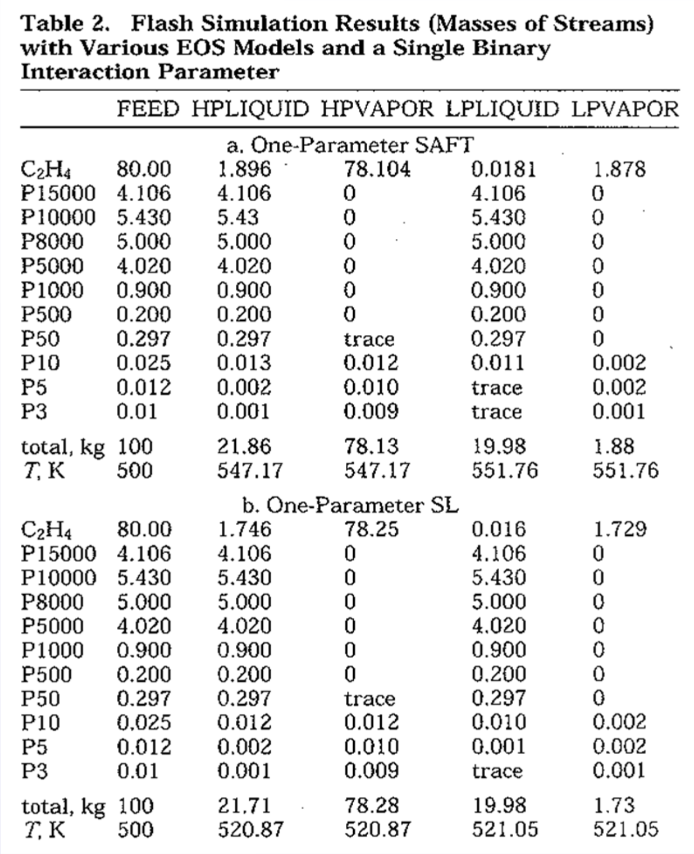
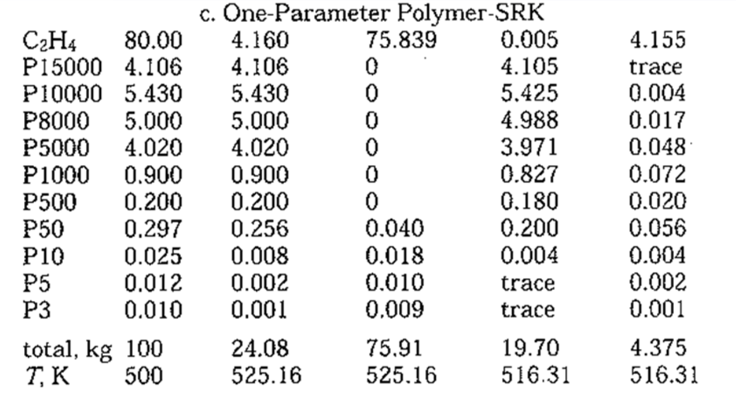


Table 2. Flash Simulation Results (Masses of Streams) with Various EOS Models and a Single Binary Interaction Parameter

	FEED	HPLIQUID	HPVAPOR	LPLIQUID	LPVAPOR
		a. One-Parameter SAFT			
C_2H_4	80.00	1.896	78.104	0.0181	1.878
P15000	4.106	4.106	0	4.106	0
P10000	5.430	5.43	0	5.430	0
P8000	5.000	5.000	0	5.000	0
P5000	4.020	4.020	0	4.020	0
P1000	0.900	0.900	0	0.900	0
P500	0.200	0.200	0	0.200	0
P50	0.297	0.297	trace	0.297	0
P10	0.025	0.013	0.012	0.011	0.002
P5	0.012	0.002	0.010	trace	0.002
P3	0.01	0.001	0.009	trace	0.001
total, kg	100	21.86	78.13	19.98	1.88
T, K	500	547.17	547.17	551.76	551.76
		b. One-Parameter SL			
C_2H_4	80.00	1.746	78.25	0.016	1.729
P15000	4.106	4.106	0	4.106	0
P10000	5.430	5.430	0	5.430	0
P8000	5.000	5.000	0	5.000	0
P5000	4.020	4.020	0	4.020	0
P1000	0.900	0.900	0	0.900	0
P500	0.200	0.200	0	0.200	0
P50	0.297	0.297	trace	0.297	0
P10	0.025	0.012	0.012	0.010	0.002
P5	0.012	0.002	0.010	0.001	0.002
P3	0.01	0.001	0.009	trace	0.001
total, kg	100	21.71	78.28	19.98	1.73
T, K	500	520.87	520.87	521.05	521.05



c. One-Parameter Polymer-SRK

C_2H_4	80.00	4.160	75.839	0.005	4.155
P15000	4.106	4.106	0	4.105	trace
P10000	5.430	5.430	0	5.425	0.004
P8000	5.000	5.000	0	4.988	0.017
P5000	4.020	4.020	0	3.971	0.048
P1000	0.900	0.900	0	0.827	0.072
P500	0.200	0.200	0	0.180	0.020
P50	0.297	0.256	0.040	0.200	0.056
P10	0.025	0.008	0.018	0.004	0.004
P5	0.012	0.002	0.010	trace	0.002
P3	0.010	0.001	0.009	trace	0.001
total, kg	100	24.08	75.91	19.70	4.375
T, K	500	525.16	525.16	516.31	516.31

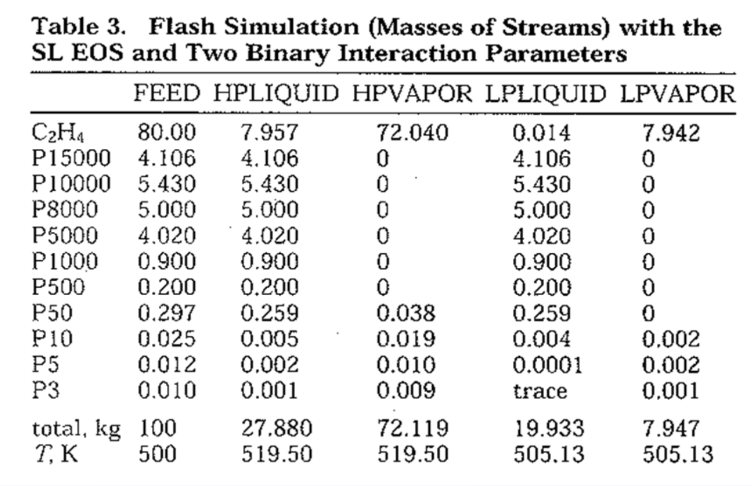


Table 3. Flash Simulation (Masses of Streams) with the SL EOS and Two Binary Interaction Parameters

	FEED	HPLIQUID	HPVAPOR	LPLIQUID	LPVAPOR
C_2H_4	80.00	7.957	72.040	0.014	7.942
P15000	4.106	4.106	0	4.106	0
P10000	5.430	5.430	0	5.430	0
P8000	5.000	5.000	0	5.000	0
P5000	4.020	4.020	0	4.020	0
P1000	0.900	0.900	0	0.900	0
P500	0.200	0.200	0	0.200	0
P50	0.297	0.259	0.038	0.259	0
P10	0.025	0.005	0.019	0.004	0.002
P5	0.012	0.002	0.010	0.0001	0.002
P3	0.010	0.001	0.009	trace	0.001
total, kg	100	27.880	72.119	19.933	7.947
T, K	500	519.50	519.50	505.13	505.13

Conclusion

- SAFT model is the most convenient from the point of availability of segment-based pure component parameters.
- For polymer-SRK we had to devise a method for the model parameters as a function of molecular size.
- For SL model a general method of estimation of pure component parameters is necessary for which no data exists.
- In general, for the polymeric molecules EOSs are very capable of prediciting the behavior of phase equilibria, yet they have some shortcomings in important areas such as the critical region.