

Modeling High-Pressure Vapor-Liquid Equilibrium for Polyethylene Industrial Systems

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Abstract

The successful description of vapor-liquid equilibrium (VLE) in solvent-polymer systems is required for devolatilization and high-pressure separation of solvent from polymer solutions. In this work high-pressure VLE industrial plant data for low density polyethylene (LDPE) and linear low density polyethylene (LLDPE) resins are used to compare the performance of Sanchez-Lacombe (SL) and Soave-Redlich-Kwong (SRK) equations of state (EOS). For SRK the mixing rules of LCVm and Wong-Sandler (WS) are tested, both coupled with Bogdanic and Vidal activity coefficient model. The results indicate the SL as the best model to describe phase behavior of these polyethylene systems under industrial conditions.

Keywords: high-pressure, vapor-liquid equilibrium, equations of state, polyethylene

1. INTRODUCTION

Linear low density polyethylene (LLDPE) is industrially produced at relatively high temperatures (200-300°C) and moderate pressures (100-300 bar) through solution polymerization. Usually some α -olefins are used as comonomers with cyclohexane as solvent. Two depressurization stages follow the reactor. The LLDPE is separated from the cyclohexane, the unreacted ethylene and comonomers in the intermediate pressure separator (IPS), where the pressure is reduced to 29.43bar. The solution that leaves the IPS bottom contains about 40 to 60 wt% of polyethylene and cyclohexane. The remaining solvent is removed in the low pressure separator (LPS). Low-density polyethylene (LDPE) is industrially synthesized at relatively high temperatures (180-300°C) and pressures (1000-3000 bar) by free-radical bulk polymerization in supercritical ethylene. In the LDPE process, an important step is the flash separation of monomers and other small molecules from the polymer produced. In the first step the reactor effluent is depressurized through a pressure reduction valve down to 150-250 bar. This allows the separation of the polymeric product from the unreacted ethylene, in a high pressure separator (HPS). The overhead monomer rich stream is cooled and recycled back to the reactor whereas the bottom polymer rich stream undergoes a second separation step at a near atmospheric pressure in a low pressure separator (LPS).

Using equations of state in phase equilibrium modeling instead of using activity coefficient models is mainly due to the recent development of a class of mixing rules that allows the use of liquid activity coefficient models in the EOS formalism. With this approach, the applicability of simple cubic EOS has been extended to complex systems such as polymeric systems, upon coupling with the appropriate activity coefficient model. Some studies in this formalism with polymer solutions can be found in the literature [1]. However,

they focus on low pressure ranges and laboratory experimental data, which are very far from the operational conditions found in industrial separation processes.

Another approach for determining phase equilibrium of polymer systems is based on the Sanchez-Lacombe EOS (SL) [2]. It can be used to predict thermodynamic properties and phase behavior of both polymeric and non polymeric systems. For vapor-liquid equilibrium, there is a lack of references in the literature [3] and none that use industrial plant data.

In this work high-pressure VLE and industrial plant data for low density polyethylene (LDPE) and linear low density polyethylene (LLDPE) resins are used to compare the performance of Sanchez-Lacombe (SL) and Soave-Redlich-Kwong (SRK) [4] equations of state (EOS). For SRK the mixing rules of LCVM [5] and Wong-Sandler (WS) [6] are tested, both coupled with Bogdanic and Vidal activity coefficient model (BV) [7]. Very recently, Costa et al. [8] carried out a detailed evaluation of several activity coefficient models both at infinite dilution and finite concentration, and the results indicated that the Bogdanic and Vidal activity coefficient model was the best one. Based on this, we chose to incorporate this activity coefficient model in the mixing rules.

2. THERMODYNAMIC MODELS

The Soave-Redlich-Kwong (SRK) equation of state is

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)} \quad (1)$$

where parameters a and b can be given by Wong-Sandler mixing rules

$$a = b \cdot \left(\sum_i \frac{x_i \cdot a_i}{b_i} + \frac{G^E}{\delta} \right) \quad (2)$$

$$b = \frac{\sum_i \sum_j x_i \cdot x_j \cdot \frac{1}{2} \cdot [(b - a/R \cdot T)_i + (b - a/R \cdot T)_j] (1 - WS_{ij})}{1 - \sum_i (a_i/b_i \cdot R \cdot T) - (G^E/\delta \cdot R \cdot T)} \quad (3)$$

δ is a numerical constant equal to $-\ln 2$ for SRK EOS and WS_{ij} is the interaction parameter.

LCVM mixing rule is given by Boukouvalas *et al.*:

$$\alpha = \frac{a}{b \cdot R \cdot T} = \sum x_i \cdot \alpha_i + \left(\frac{\lambda}{A_v} + \frac{1-\lambda}{A_M} \right) \cdot \frac{G^E}{R \cdot T} + \frac{1-\lambda}{A_M} \cdot \sum x_i \cdot \ln \left(\frac{b}{b_i} \right) \quad (4)$$

with $A_v = \ln 2$ and $A_M = -0.53$ for SRK EOS and λ is 0.36. The classical linear mixing rule is used for parameter b .

LCVM and Wong-Sandler mixing rules need a G^E model and the recommended one is the BV model, whose segment activity coefficients are calculated through the UNIQUAC model and contains an interaction parameter UQ_{ij} .

The Sanchez and Lacombe EOS [5] is given by:

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T} \cdot \left[\ln(1 - \tilde{\rho}) + \left(1 - \frac{1}{r} \right) \cdot \tilde{\rho} \right] = 0 \quad (5)$$

$$\tilde{T} = \frac{T}{T^*} \quad \tilde{P} = \frac{P}{P^*} \quad \tilde{\rho} = \frac{\rho}{\rho^*} \quad (6)$$

$$T^* = \frac{\varepsilon^*}{k} \quad P^* = \frac{\varepsilon^*}{v^*} \quad \rho^* = \frac{MW}{rv^*} \quad (7)$$

where T is the absolute temperature, P is the pressure, ρ is the density, MW is the molecular weight, k is the Boltzmann constant, and r , ε^* , and v^* are pure component parameters related to the corresponding scale factors T^* , P^* , ρ^* , respectively. For mixtures, the model parameters are composition dependent. The binary interaction parameters $SL1_{ij}$ and $SL2_{ij}$ are related to the cross parameters.

3. RESULTS AND DISCUSSION

The polymer is assumed to be monodisperse for all systems. The pure component parameters and segment parameters of polymer for SL EOS are taken from Sandler et al. [9] and to perform calculations with the SRK equation of state for polymers, the pure parameters are calculated following Kontogeorgis's method [10].

We selected eight resins to study the several aspects of the LDPE flash separation. Table 1 shows the resins characteristics and the HPS operational conditions. Table 2 presents the LLDPE resins type according to the following contents of the reactor feed: ethylene and cyclohexane (LLDPE-A); ethylene, 1-butene and cyclohexane (LLDPE-B); ethylene, 1-octene and cyclohexane (LLDPE-C); ethylene, 1-butene, 1-octene and cyclohexane (LLDPE-D). Each type is numbered to indicate its pressure and temperature operational conditions.

Table 1 LDPE molecular weight and HPS separator operational conditions

Resin	Mw (g/mol)	T_{HPS} (°C)	P_{HPS} (bar)	T_{HPS} (°C)	P_{HPS} (bar)
LDPE-1	335000	280.29	250.06	241.04	0.35
LDPE-2	295200	278.80	251.90	239.49	0.42
LDPE-3	181000	230.29	249.88	212.17	0.37
LDPE-4	166000	253.03	250.55	226.73	0.46
LDPE-5	340000	237.68	249.87	217.91	0.42
LDPE-6	322000	277.17	249.54	242.73	0.41
LDPE-7	236600	247.92	254.00	224.93	0.40
LDPE-8	426300	265.33	253.28	235.69	0.42

Binary interaction parameters of the various models are fitted to industrial operational data and the Nelder-Mead simplex method [11] is applied to minimize the objective function based on mass the mass composition of component.

Simulation of HPS behavior for LDPE resin and comparison of the equation of state performances allow concluding that Sanchez-Lacombe EOS is the best choice. Further, it is simpler to use and its capacity to describe parameter dependence on polymer molecular weight is more accurate.

Two of the four models are able to simulate the IPS in LLDPE industrial plant: Sanchez-Lacombe and SRK-WS. A comparison, demonstrated the best results are obtained with Sanchez-Lacombe EOS, independent the specific component considered.

Table 2 LLDPE resins and IPS operational conditions

Resin	T (°C)	P (bar)	Resin	T (°C)	P (bar)
LLDPE-A1	269.93	31.70	LLDPE-B5	266.11	29.55
LLDPE-A2	269.21	30.54	LLDPE-B6	258.64	31.29
LLDPE-A3	271.80	30.87	LLDPE-B7	256.07	30.65
LLDPE-A4	275.90	30.90	LLDPE-B8	262.79	31.12
LLDPE-A5	271.60	30.71	LLDPE-B9	259.64	31.88
LLDPE-A6	275.96	30.58	LLDPE-B10	256.57	29.06
LLDPE-A7	273.34	31.32	LLDPE-B11	263.48	30.74
LLDPE-A8	277.05	31.61	LLDPE-B12	267.46	31.05
LLDPE-B1	258.02	31.49	LLDPE-C1	275.26	29.46
LLDPE-B2	259.64	32.02	LLDPE-D1	267.08	27.90
LLDPE-B3	256.75	31.44	LLDPE-D2	268.38	30.86
LLDPE-B4	258.06	31.17	LLDPE-D3	268.02	29.58
			LLDPE-D4	274.41	28.43

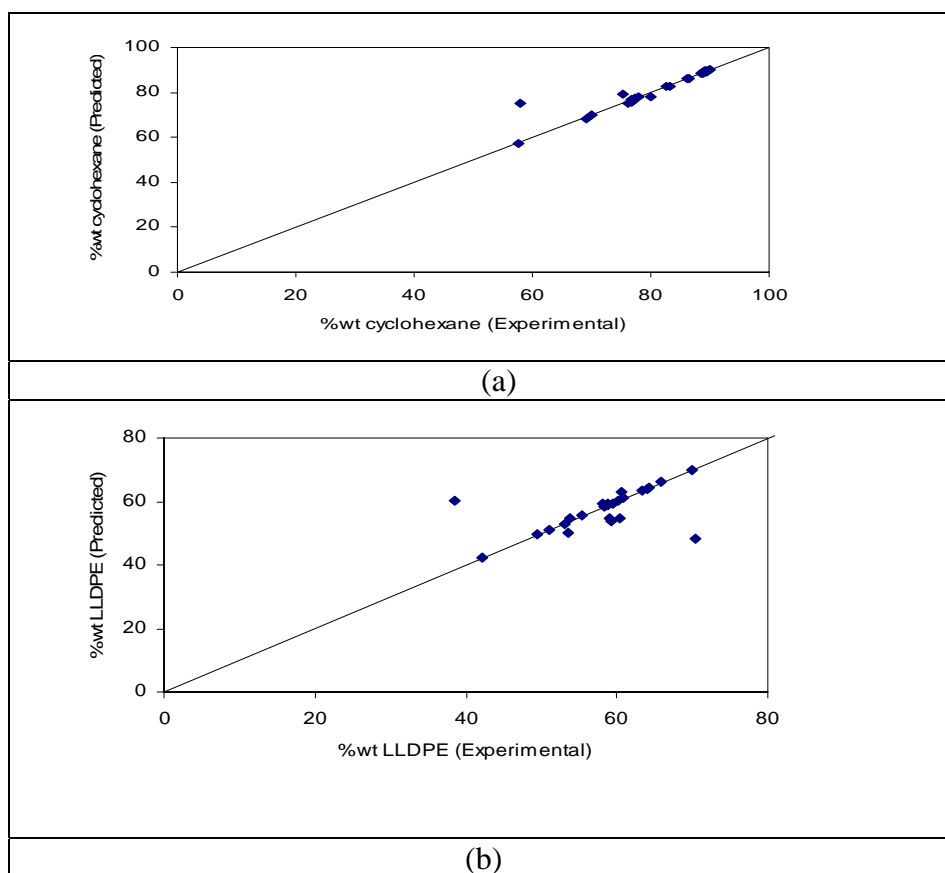
**Fig. 1.** IPS overhead (a) and bottom (b) compositions for LLDPE resin: Experimental and predicted data by SL EOS.

Figure 1 shows the results for IPS overhead and bottom compositions for 25 LLDPE resins obtained with SL. Figure 1 a presents the overhead composition for cyclohexane predicted by SL. In these cases, the most important component to be monitored is cyclohexane, because it is the solvent and, as a consequence, it is present in all resins, with the highest concentration values. The results indicate a quite good simulation not only for cyclohexane but also for the other components. Figure 1b shows the bottom composition for LLDPE. At the bottom stream, cyclohexane and LLDPE are the key components, since their concentrations achieve the highest values. It can be seen that SL EOS offers good accuracy for simulation in this pressure range.

As previously described, for HPS it is important to evaluate both overhead and bottom streams. The amount of ethylene in the overhead is about 99% in a mass basis. The bottom usually contains about 20% of ethylene and 80% of LDPE fractions. Figure 2 show the results for HPS overhead composition for LDPE resin obtained with SL. The results indicate the best prediction of overhead and bottom composition for 7 of the 8 tested resins using SL EOS. The worst results in overhead are to RES-6 and in bottom are to RES-5 .Thus, SL EOS is also the best model do describe the HPS operational conditions and system properties. The results of simulation with SRK-LCVM and SRK-WS for HPS indicate that the overhead stream is formed by pure ethylene. As a consequence, only the bottom composition can be discussed with these models.

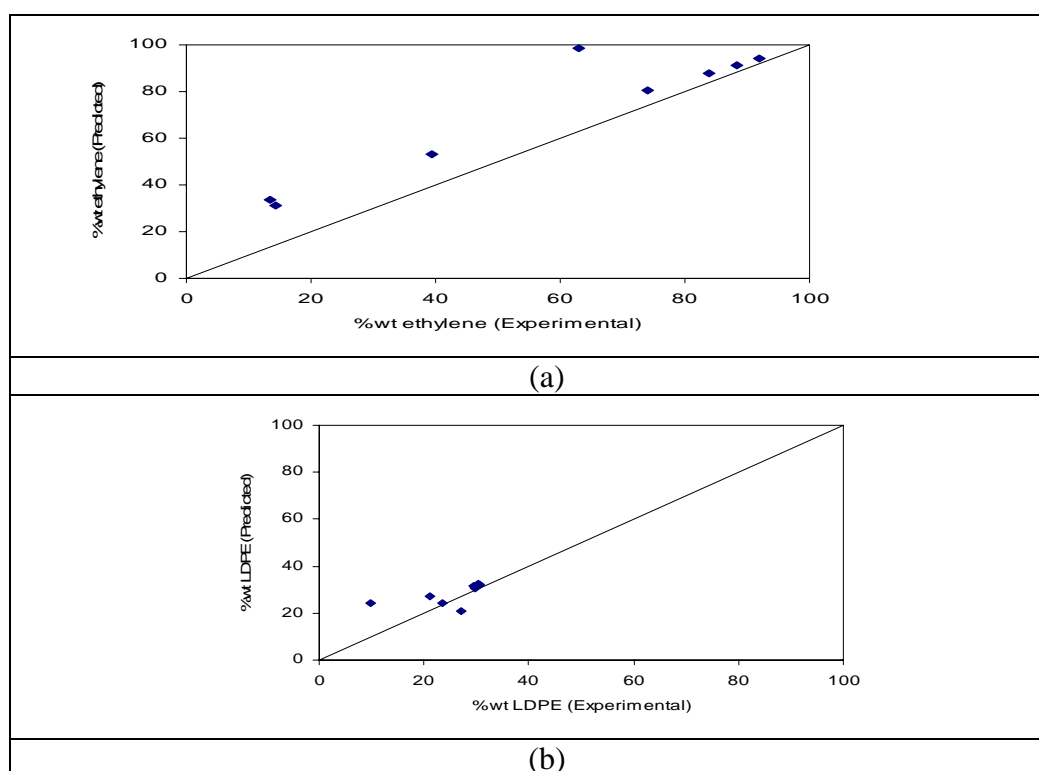


Fig. 2. HPS overhead (a) and bottom (b) compositions for LDPE resin: Experimental and predicted data by SL EOS.

4. CONCLUSIONS

To simulate the flash HPS and IPS separators in the industrial polyethylene process, low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE) resin industrial plant data are used to test Sanchez-Lacombe (SL) and Soave-Redlich-Kwong

(SRK) EOS performance. For the SRK EOS, three different mixing rules are compared: van der Waals (VDW) one fluid, LCVM and Wong-Sandler (WS). The Bogdanic and Vidal activity coefficient model is used coupled with LCVM and Wong-Sandler mixing rules. To estimate the pure polymer parameters in the SRK equation of state, the Kontogeorgis procedure is used coupled with the GCVOL method.

The results for the HPS and IPS separators indicate that the SL EOS is the best model. This conclusion is based on the comparison of predicted and experimental data for mass composition, as well as the constant values estimated for the interaction parameters of this equation.

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