STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, LIV, 2, 2009

DON'T GAMBLE WITH PHYSICAL PROPERTIES OF POLYMERS

ANTON A. KISS[a], ALEXANDRE C. DIMIAN[b], PIET D. IEDEMA[b]

ABSTRACT. This study investigates several possible thermodynamic options (Sanchez-Lacombe, SAFT, Flory-Huggins, Soave-Redlich-Kwong) available in designing polymerization systems. Various results are predicted by these models with respect to monomer-polymer separation and polymer properties. These results show that it is essential to choose the proper thermodynamic model in order to get reliable results from simulation. The low density polyethylene (LDPE) process is presented as an industrial case study.

Keywords: *polymerization systems, property model polymers, LDPE*

INTRODUCTION

Process system engineers use computer simulations to perform a variety of tasks, ranging from calculations of mass and energy balances to rating, sizing, optimization, dynamics modeling and performance evaluation of process alternatives that could reduce investment and operating costs. Nowadays, due to significantly improved computing power, an engineer can relatively quickly set up the basic simulation specifications (including the physical properties), process conditions and define a complex flowsheet. However, note that the solid base of any process modeling and simulation is represented by the physical properties models. Missing or inadequate physical properties can undermine the accuracy of a model or even prevent one from performing the simulation. Finding good values for inadequate or missing physical property parameters is the key to a successful simulation. Nevertheless, this depends strongly upon choosing the right estimation methods – issue already recognized in the world of chemical processes modeling by the axiom "*garbage in, garbage out"* which means that the simulation results have the same quality as the input data / parameters [1].

[a] *AkzoNobel, Research and Technology Center, Velperweg 76, 6824 BM, Arnhem, The Netherlands, tony.kiss@akzonobel.com*
[b] *University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands, a.c.dimian@uva.nl, p.d.iedema@uva.nl*

This article investigates the properties models most used in polymerization systems, by performing regressions and parameters fitting, and show by an industrial LDPE case study that different results are predicted with respect to monomer-polymer separation and polymer properties.

PROBLEM STATEMENT

In any polymerization system there is a separation of the polymer from monomer, which is recycled in case of incomplete conversion. Although the monomer-polymer separation may appear easy, this is not a trivial task because mixtures of small molecules and long-chain polymers are involved [2]. Therefore it is of utmost importance to opt for the suitable method in order to get reliable and meaningful results from the simulation.

The problem is how to select the right property model for which reliable parameters can be calculated, when insufficient experimental data is available. To solve this problem we investigate the most used properties models (e.g. Sanchez-Lacombe, SAFT, Flory-Huggins, Poly-SRK) available in polymerization systems, perform regression and parameter fitting, and show – by an industrial relevenat case study – that different results are predicted with respect to monomer-polymer separation and polymer properties. The property models used in this work describe with good accuracy the behavior of both conventional molecules and polymer chains.

As both conventional molecules and polymers are present in the process, the key physical properties of all types of molecules must be predicted with acceptable accuracy by the models used. A major advantage of using equation-of-state (EOS) is that pure-component parameters of many conventional molecules encountered in polymer processes are already available in literature [3,4]. Nevertheless there is a need to estimate somehow the binary interaction parameters for these models. Note that if the binary parameters are not fitted to experimental data all the models tested revealed unsatisfactory performance.

RESULTS AND DISCUSSION

In this work the high-pressure low-density poly-ethylene (HP-LDPE) system was selected as case study [5,6]. The flowsheet of this process as well as the most important specifications are shown in Figure 1. Ethylene is fed at 100℃ and 2025 bar to the mixing section, where the recycle is added. The mixed stream is heated in a pre-heater where the temperature increases to 170℃. The heated stream is passed then through the tubular polymerization reactor (6 cm diameter and 940 m length).

The initiator (benzoyl peroxide) is fed at two different locations: reactor inlet and half of the reactor length. The reaction mixture leaves the reactor and goes to the high-pressure separation (HPS) flash operated at 250 bar. Here, about 95% of the monomer is separated and sent to the recycle mixer. The second flash is the low-pressure separator (LPS) that makes the final separation at 2 bar. The rest of the monomer is sent to the recycle mixer, while the LDPE is recovered at the bottom, at purity higher than 99%. The high- and low-pressure recycles of monomer are mixed, and then re-compressed at the same pressure as the fresh ethylene stream. The recycle is then mixed with fresh ethylene and fed again to the reactor.

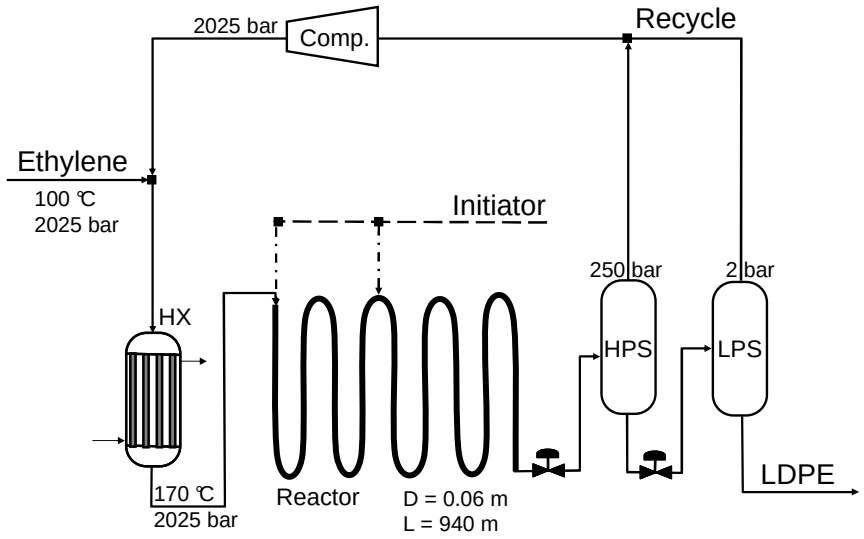

Figure 1. Flowsheet of the high-pressure LDPE process.

Experimental data was used to calculate the model parameters. The parameters should be segment-based or scalable for the size of the polymer. This condition is necessary because the size of the polymer changes in the process, and the model used must be able to accommodate this fact. Different results are predicted by the EOS models with respect to monomer-polymer separation and polymer properties. This has a major impact on the results of the simulation of a certain design. The results presented in this work for the LDPE system are an effective starting point in approaching other polymerization systems as well. Note that all calculations, including an industrial reactor simulations, were rigorously performed using the state-of-the-art software Aspen Polymers Plus that is a layered product built on top of AspenTech AspenPlus [7,8].

Note that each EOS properties model has exclusive characteristics that affect the results of modeling the pure monomer and polymer mixture behavior. Out of the four EOS models used, Sanchez-Lacombe and Poly-SRK EOS produced the best acceptable fit of the data. Both models are capable of predicting properties at both high and low-pressure, and give accurate results especially for high temperatures.

Table 1 lists the TPXY binary vapor-liquid equilibrium (VLE) data of the mixture ethylene-polyethylene (with number average molecular weight MW_n = 31700, and weight average MW = 247800) that have been used for regression [9]. The model parameters were calculated by regressing the experimental data.

Table 1. TPXY binary VLE data of the mixture ethylene-polyethylene

Temp. / K	Pressure / KPa	X, Ethylene	X, PE	Y, Ethylene	Y, PE
399.15	455.8	0.0018	0.9982	1	0
399.15	790.30	0.0037	0.9963	1	0
399.15	1135	0.0055	0.9945	1	0
399.15	1479	0.0075	0.9925	1	0
399.15	1824	0.0107	0.9893	1	0
399.15	2168	0.0136	0.9864	1	0
399.15	2513	0.0158	0.9842	1	0
399.15	2857	0.0175	0.9825	1	0
399.15	3202	0.0198	0.9802	1	0
399.15	3546	0.0221	0.9779	1	0
399.15	3891	0.0242	0.9758	1	0
399.15	4235	0.0255	0.9745	1	0
399.15	4580	0.0285	0.9715	1	0
399.15	4924	0.0305	0.9695	1	0
399.15	5269	0.0330	0.9670	1	0
399.15	5613	0.0359	0.9641	1	0
413.15	455.8	0.0015	0.9985	1	0
413.15	790.3	0.0034	0.9966	1	0
413.15	1135	0.0048	0.9952	1	0
413.15	1479	0.0068	0.9932	1	0
413.15	1824	0.0087	0.9913	1	0
413.15	2168	0.0112	0.9888	1	0
413.15	2513	0.0131	0.9869	1	0
413.15	2857	0.0151	0.9849	1	0
413.15	3202	0.0166	0.9834	1	0
413.15	3546	0.0189	0.9811	1	0
413.15	3891	0.0208	0.9792	1	0
413.15	4235	0.0235	0.9765	1	0
413.15	4580	0.0250	0.975	1	0
413.15	4924	0.0277	0.9723	1	0
413.15	5269	0.0296	0.9704	1	0
413.15	5613	0.0328	0.9672	1	0

Temp. / K	Pressure / KPa	X, Ethylene	X, PE	Y, Ethylene	Y, PE
428.15	455.8	0.0013	0.9987	1	0
428.15	790.30	0.0029	0.9971	1	0
428.15	1135	0.0039	0.9961	1	0
428.15	1479	0.0055	0.9945	1	0
428.15	1824	0.0074	0.9926	1	0
428.15	2168	0.0090	0.991	1	0
428.15	2513	0.0105	0.9895	1	0
428.15	2857	0.012	0.988	1	0
428.15	3202	0.0146	0.9854	1	0
428.15	3546	0.0164	0.9836	1	0
428.15	3891	0.0178	0.9822	1	0
428.15	4235	0.0207	0.9793	1	0
428.15	4580	0.0222	0.9778	1	0
428.15	4924	0.0242	0.9758	1	0
428.15	5269	0.0265	0.9735	1	0
428.15	5613	0.0286	0.9714	1	0

Table 2. Unary parameters for Sanchez-Lacombe EOS

Parameter Name / Element	Symbol	Units	Ethylene	PE
SLTSTR	T^*	K	291	673
SLPSTR	P^*	bar	3339	4250
SLRSTR	ρ^*	Kg / m^3	660	887

Table 3. Binary parameters for Sanchez-Lacombe EOS

Parameter	Comp. i	Comp. j	Value (SI units)	Stand.-dev.
SLKIJ/1 (k_{ij})	PE	Ethylene	-0.09	0
SLETIJ/1 (η_{ij})	PE	Ethylene	-0.4040175	0.00428089

Table 4. Parameters of SAFT model

Parameter Name	Symbol	Ethylene	PE	$C_{14}H_{10}O_4$	$C_8H_{18}O_2$	Water
SAFTM	m	1.464	1133.72	11.993	7.51	1.54
SAFTV	v^{00}	18.157	12.0	12.13	12.30	14.14
SAFTU	u^0/k	212.06	228.36	208.93	206.17	188.86
SFTEPS	e/k	10	10	10	10	1

Table 5. Regressed binary parameters of SAFT model

Parameter	Comp. i	Comp. j	Value (SI units)	Stand.-dev.
SFTKIJ (k_{ij})	PE	Ethylene	0.08563059	0.00256897
SFTLIJ (l_{ij})	PE	Ethylene	0.00128981	0.00011733

Table 6. Mathias-Copeman constants required by the SRK-EOS model

Parameter	Comp. i	Comp. j	Value (SI units)	Stand. Dev.
FHCHI/1	PE	ethylene	5.929	0.657
FHCHI/2	PE	ethylene	-1437.673	272.593

Table 7. Parameters of the SRK-EOS model

Parameter Name / Element	Component	Value (SI units)
$T_{c,i}$	ethylene	303.211224
$P_{c,i}$	ethylene	130.667512
$T_{c,i}$	PE	1545.17701
$P_{c,i}$	PE	32.841247

Parameter Name / Element	Symbol	Ethylene	PE
RKSMCP / 1	$C_{l,1}$	0.656855	1
RKSMCP / 2	$C_{l,2}$	-0.362904	0
RKSMCP / 3	$C_{l,3}$	0.676711	0

For the **Sanchez-Lacombe** EOS the unary parameters (for ethylene and poly-ethylene) shown in table 2 were used. By fitting the experimental data presented in Table 1 the binary parameters (k_{ij} and η_{ij}) of the Sanchez-Lacombe EOS for the binary mixture ethylene-polyethylene have been regressed (Table 3).

The three unary parameters v^{00}, u^0 / k, and m for each component represent the necessary user input to apply ***Statistical Associating Fluid Theory (SAFT)*** to real fluid systems (together with the value of e/k). For fine tuning of mixture phase behaviour, the binary parameters k_{ij} and l_{ij} can be regressed to available phase equilibrium data. The values of these binary parameters are usually close to zero. The SAFT model parameters and their values are listed in Table 4.

The segment energy u^0/k and the segment volume v^{00} are *segmental parameter*s, which suggest that they should remain fairly constant between components in the same homologous series. The third parameter m represents the number of segments on the chain; this implies that m should be proportional to the molecular mass. In the case of normal alkanes, Huang and Radosz proposed the following generalized correlations for the pure-component parameters [10]:

$$m = 0.70402 + 0.046647 \cdot MW \quad (1)$$

$$mv^{00} = 11.888 + 0.55187 \cdot MW \quad (2)$$

$$u^0 / k = 210 - 26.886 \cdot e^{-0.013341 \cdot MW} \quad (3)$$

The unary parameters (m, v^{00} and u^0/k) for the initiators and water were calculated using the above equations. The regressed binary parameters k_{ij} and l_{ij} of the SAFT EOS are presented in Table 5.

The binary parameters α_{ij} and β_{ij} of the ***Flory-Huggins*** activity coefficient model for the binary mixture ethylene-polyethylene have been found by regressing the same set of experimental data. For the unary parameters of ethylene and polyethylene we had to use the default value (one) in our data regression simulation (DRS).

In order to use the polymer ***Soave-Redlich-Kwong (SRK)*** EOS, the pure components parameters needed are the critical constants T_c, P_c and the Mathias-Copeman constants. Tables 6 and 7 present the unary and binary parameters of the models.

Polymers are not supposed to vaporize, and therefore for the critical temperature of the polymers a high value is recommended (typically T_c > 1000 *K*). For the same reason, a relatively low critical pressure is needed ($P_c < 10^6$ N/m^2). For all of the Mathias-Copeman parameters for oligomers and polymers, zero is recommended due to unavailability of information on polymer vapor pressure.

The identification of the model parameters requires the regression of the parameters $T_{c,i}$ and $P_{c,i}$ (critical temperature and critical pressure respectively) for ethylene and polyethylene. To this end the TPXY binary vapor-liquid-equilibrium data of ethylene-polyethylene, together with the Mathias-Copeman parameters (for ethylene and PE) have been used.

The results of the data regression simulations for all models considered are presented in Figure 2. The lines (solid, short- and long-dashed) represent the regressed equations while the dots represent the experimental values. In all cases, there is a good agreement between the predictive model and the experimental data, both at high and low-pressure and especially at higher temperatures. Yet, note that practically it is almost impossible to get accurate experimental data at supercritical conditions.

Figure 3 shows that different polydispersity (A, B and C) and reactor temperature profiles (D) are predicted by the property models investigated. This has a significant impact on the results of the simulation of a certain polymerization process design. For example, the final polydispersity index predicted by Sanchez-Lacombe and SAFT is ~6 (Figure 3B), while Florry-Huggins and SRK-EOS predict a PDI of ~2.5 (Figure 3A and 3C) – these figures corresponding to different end properties of the LDPE polymer. In terms of temperature the differences can be as high as 100 °C, thus making the design of an efficient reactor cooling system questionable (Figure 3D). The comparison of the simulated results with industrial data for the LDPE processes shows that the SRK-EOS provides the best estimates; hence Poly-SRK EOS should be used for reliable simulations of LDPE.

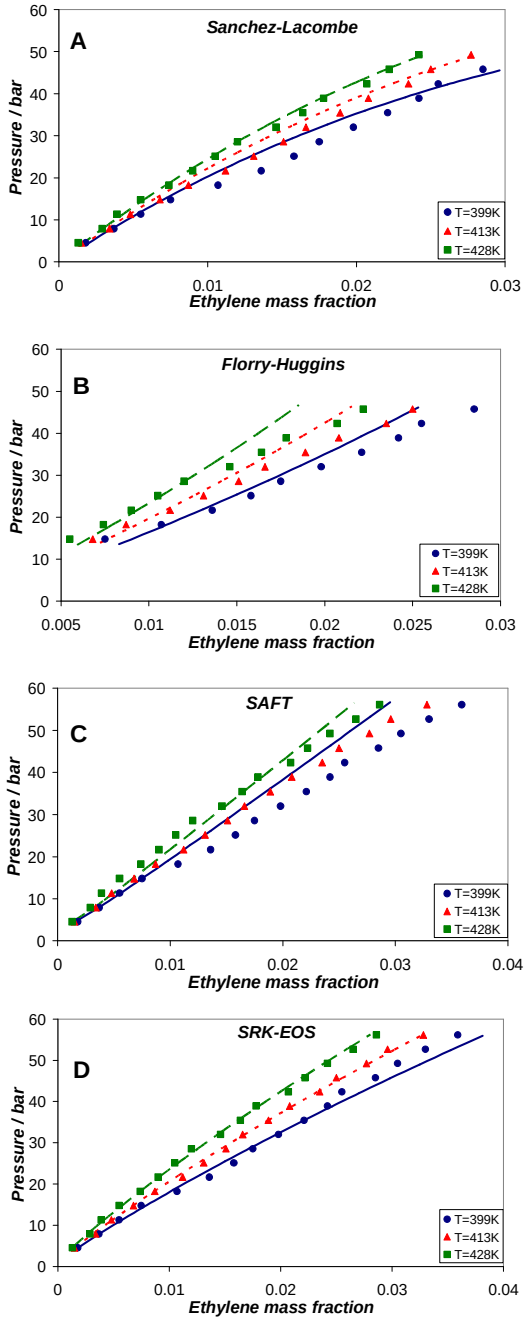

Figure 2. Vapor pressure vs mass fraction of ethylene, regressed and experimental data.

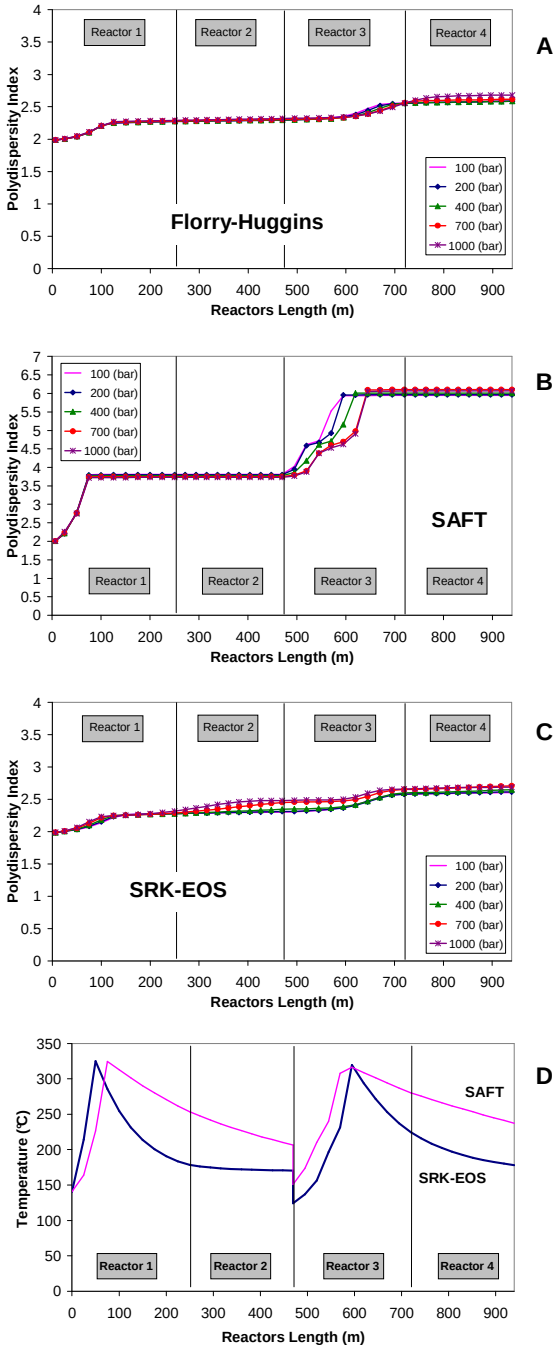

Figure 3. Polydispersity index (PDI) and reactor temperature profiles.

CONCLUSIONS

As both conventional molecules and polymers are present in the process, the key physical properties of all types of molecules must be predicted with acceptable accuracy by the thermodynamic models used.

Using an EOS has the advantage that pure-component parameters of many conventional molecules encountered in polymer processes are already available in literature. Yet, there is a need to estimate the binary interaction parameters for these models. If the binary parameters are not fitted to experimental data all models reveal unsatisfactory performance.

This study shows that all models offer a good fit of the data for the binary mixture ethylene-polyethylene. However, different monomer-polymer properties are predicted by the models investigated in this work. This has a significant impact on the results of the simulation of a certain polymerization process design. For the industrial LDPE case study the predicted reactor profiles have relatively large differences in the polydispersity index and the reaction temperature. Based on the comparison of the simulated results with data from the industrial plant, the Poly-SRK EOS proved to give the most reliable estimates. Note that the results presented in this work can be also used as a starting point in approaching other polymerization systems.

ACKNOWLEDGMENTS

We thank Abdelghani Belkou, as well as Aspen Technology for the excellent technical support.

NOTATION

MW – Weight average molecular weight
MW_n – Number average molecular weight
PDI – Polydispersity index (PDI), PDI = MW / MW_n
P – Pressure, bar
P_c – Critical pressure, bar
T – Temperature, K
T_c – Critical temperature, K
X – Mass fraction in liquid phase
Y – Mass fraction in vapor phase
α_{ij}, β_{ij} – Binary interaction parameters (BIP), Flory-Huggins
k_{ij}, η_{ij} – Binary interaction parameters (BIP), Sanchez-Lacombe
k_{ij}, l_{ij} – Binary interaction parameters (BIP), SAFT
ρ – Density, kg / m^3
m – Number of segments on the chain
u^0/k – Segment energy
v^{00} – Segment volume

REFERENCES

1. E. C. Carlson, *Chemical Engineering Progress*, **1996**, *10*, 35.
2. A. A. Kiss, S. P. Agachi, *Hungarian Journal of Industrial Chemistry*, **1999**, *27*, 117.
3. H. Orbey, C. P. Bokis, C. C. Chen, *Industrial and Engineering Chemistry Research*, **1998**, *37*, 1567.
4. H. Orbey, C. P. Bokis, C. C. Chen, *Industrial and Engineering Chemistry Research*, **1998**, *37*, 4481.
5. A. A. Kiss, C. S. Bildea, A. C. Dimian, P. D. Iedema, *Chemical Engineering Science*, **2002**, *57*, 535.
6. A. A. Kiss, C. S. Bildea, A. C. Dimian, P. D. Iedema, *Chemical Engineering Science*, **2003**, *58*, 2973.
7. AspenTech Inc., *Aspen Polymers Plus 2004.1 – User Guide*, vol. 1 and 2, **2004**.
8. AspenTech Inc., *Aspen Polymers Plus 2004.1 – Examples & Applications*, **2004**.
9. W. Hao, H. S. Elbro, P. Alessi, *Chemistry Data Series*, XIV, DECHEMA **1992**.
10. H. H. Stanley, M. Radosz, *Industrial and Engineering Chemistry Research*, **1990**, *29*, 2284.