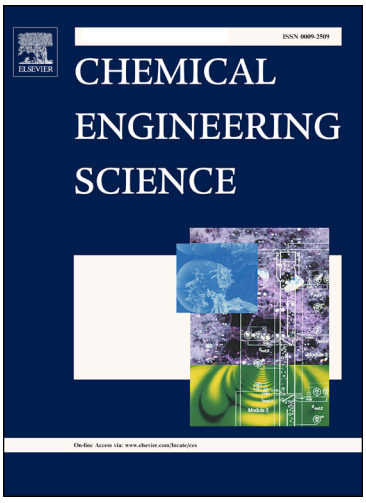

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PII: S0009-2509(18)30604-3
DOI: https://doi.org/10.1016/j.ces.2018.08.033
Reference: CES 14448

To appear in: *Chemical Engineering Science*

Received Date: 3 March 2018
Revised Date: 22 July 2018
Accepted Date: 14 August 2018

Please cite this article as: M. Glass, H. Djelassi, A. Mitsos, Parameter Estimation for Cubic Equations of State Models Subject to Sufficient Criteria for Thermodynamic Stability, *Chemical Engineering Science* (2018), doi: https://doi.org/10.1016/j.ces.2018.08.033

Parameter Estimation for Cubic Equations of State Models Subject to Sufficient Criteria for Thermodynamic Stability

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Abstract: A formulation for parameter estimation in cubic equations of state (CEOS) models for phase equilibrium thermodynamics is proposed. This formulation *guarantees* for the regressed parameters that the predicted mole fractions correspond to stable equilibria, when standard methods fail and demonstrably entail erroneous process simulation results. The present formulation overcomes these deficiencies, which is predicated on a bilevel structure extending Mitsos et al. (*Chem. Eng. Sci.*, 64:548-559, 2009). That is, an upper-level (parameter fitting) problem is minimized, subject to multiple lower-level problems, which encode thermodynamic stability. The CEOS constitutes an equality constraint on the lower level, which adds to the difficulty of the bilevel program. For the VLE of C_5H_{12}/H_2S, it is demonstrated that the method permits an acceptable fit with physically sensible CEOS root values. Thus, the regressed parameter values may be applied to, e.g., process simulation.

Keywords: cubic equation of state, data regression, bilevel program, tangent criterion, false liquid-liquid split

Abbreviations: bilevel program (BLP), cubic equation of state (CEOS), equality constraint (EC), inequality constraint (IC), Karush-Kuhn-Tucker (KKT), lower bound (LBD), lower-bounding problem (LBP), left-hand side (LHS), Linear Independence Constraint Qualification (LICQ), liquid-liquid equilibrium (LLE), lower-level problem (LLP), mixed-integer nonlinear program (MINLP), nonlinear program (NLP), Non-Random Two Liquid (NRTL), Perturbed Chain - Statistical Associated Fluid Theory (PC-SAFT), Peng-Robinson CEOS (PR), right-hand side (RHS), Redlich-Kwong CEOS (RK), semi-infinite program (SIP), Soave-Redlich-Kwong CEOS (SRK), tangent plane distance function (TPD), Trebble-Bishnoi CEOS (TB), upper bound (UBD), Universal Quasichemical Functional Group Activity Coefficients (UNIFAC), vapor-liquid(-liquid) equilibrium (VL(L)E), upper critical solution temperature (UCST)