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Construction of a Minimum Energy Path for the VT Flash Model by the String Method Coupled with the Exponential Time Differencing Scheme

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Abstract. Flash calculation plays significant roles in petroleum and chemical industries. Since Michelsen proposed his milestone studies in 1982, through several decades of development, the current research interests on flash calculation have been shifted from accuracy to efficiency, but the ultimate goal remains the same; that is accurate determination of equilibrium phase amounts and compositions at a given condition. On the other hand, finding the transition route and its related saddle point is often crucial to understand the whole energy landscape of flash models, which would provide new insights for designing numerical algorithms or optimizing existing ones. In this study, an efficient numerical approach is developed by coupling the string method with the exponential time differencing (ETD) scheme to investigate the minimum energy paths and first-order saddle points of VT flash models with Peng-Robinson equation of state. As a promising alternative to the conventional approach, VT flash calculates phase equilibria under a new variable specification of volume and temperature. The Rosenbrock-type ETD scheme is used to reduce the computational difficulty caused by the high stiffness of the model systems. The proposed ETD-String method successfully calculates the minimum energy paths of single-component and two-component VT flash models with strong stiffness. Numerical results also show good feasibility and accuracy in calculation of equilibrium phase amounts and compositions.

Key words: VT flash, Peng-Robinson equation of state, minimum energy path, string method, Rosenbrock-type exponential time differencing scheme.

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1 Introduction

Accurate knowledge of phase equilibria is of vital importance in petroleum industry to determine the number of equilibrium phases and their amounts and compositions for complex reservoir fluids, which stimulates the development of equation-of-state-based flash calculation. One important application of flash calculation is modeling phase behaviors of hydrocarbon mixtures in compositional flow simulators, which are mainly used to model recovery processes sensitive to compositional changes, such as miscible flooding [1]. Moreover, it is often used as standalone calculation as well to analyze, design and optimize processes and facilities, such as reducing undesired species (e.g. H_2O) for conforming to product specifications, removing acid gas (e.g. CO_2 and H_2S) for protecting pipelines and equipment from corrosion [2–4], determining the amount of inhibitor (e.g. methanol and glycols) for avoiding gas hydrate formation [5–8], controlling asphaltene precipitation for enhancing flow assurance [9–11], etc.

The most commonly-used flash model of a M components system is formulated under the specified pressure (P), temperature (T) and chemical composition ($\boldsymbol{N} = [N_1,\cdots,N_M]$), which is known as PT flash calculation in petroleum industry. Usually, the Wilson correlation is used to initialize flash calculation but this approximation does not guarantee convergence to the equilibrium solution. To overcome this issue, stability test is applied which gives a better initial approximation but meanwhile requires additional computational cost. The milestone studies of Michelsen in stability testing [12] and phase splitting calculation [13] laid a foundation for the development of PT flash calculation using a single consistent equation of state (EOS), such as the Soave-Redlich-Kwong (SRK) EOS [14] and the Peng-Robinson (PR) EOS [15].

Recently, the computation of phase equilibria under the given volume (V), temperature (T) and mole composition ($\boldsymbol{N}$), also known as VT flash calculation, has become a promising alternative to the conventional PT flash model. In addition to its well-posed formulation, VT flash exhibits a unique pressure-volume relation so that the root selection procedure in PT flash framework can be avoided [16]. Another important advantage of VT flash formulation is modeling phase behaviors of unconventional reservoir fluids with noneligible capillary effect [17–19], given that the commonly-used interfacial tension models are explicit functions of molar density rather than pressure. Moreover, it is straightforward to use VT flash to model complex fluid mixtures that contain associating fluid, like H_2O, since the association contribution is originally defined based on Helmholtz free energy. During the past few years, numerous efforts have been made to expand the applications of VT flash calculation not only in various phase equilibria problems [20–22] but also in compositional flow simulation [23].

The aforementioned flash calculations mainly focus on the determination of phase amounts and compositions at the equilibrium state where either the Gibbs free energy or Helmholtz free energy is minimized at the end of PT or VT flash calculation. In principle, the equilibrium state calculated by the classical flash framework is usually a local minimum of the energy landscape, but there is no guarantee it is the one with the lowest en-