Meeting report

Tasks assigned:

- Task 1: Re-visit the explanation for why the derivative of capillary pressure should be set to zero during the minimization of the TPD with capillary pressure.
- Task 2: Derive a method for updating the composition and molar volume / mole numbers as a combined stability analysis/phase split calculation.
- Task 3: Do a manual combined stability analysis and phase split calculation.
- Task 4: Describe and implement the stability analysis algorithm in component molar density to a saturation dependent capillary pressure model.

Status of tasks:
- Task 1: Done
- Task 2: Done
- Task 3: Done
- Task 4: In progress

Summary of results:

Task 1: Re-visit the explanation for why the derivative of capillary pressure should be set to zero during the minimization of the TPD with capillary pressure
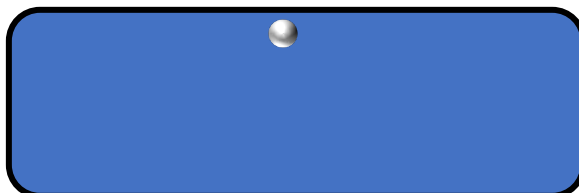

Figure 1 - PVT cell with single bubble appearing at the top of the cell indicating instability

The stability analysis in component molar density space can be thought of as looking for a composition and volume such that an infinitely small bubble of 0 volume would produce a negative TPD value. The system is specified at a constant temperature, volume, and composition therefore, during the stability analysis, the total volume and number of moles should not be allowed to change. When evaluating the derivative of capillary pressure with respect to component molar density d_i, it is assumed that the volume of that bubble is allowed to increase or decrease. When that is done at the stationary point, it violates the specifications of the problem related to constant total volume, and number of moles for each component. Therefore, we must

set the capillary pressure to be constant during the TPD minimization. The gradient of the TPD function with Helmholtz in d_i space then becomes:

$$\frac{\partial \overline{D}^{ST}}{\partial d_i} = \left(\ln\left(f_i(\vec{d})^{SP} \right) - \ln\left(f_i^{ref} \right) \right)$$

The exponent SP refers to the phase corresponding to the stationary point found by the stability analysis.

Alternative explanation:

What the extra term in the gradient does is transform the function on which the stability analysis. When it is used, there is actually only one tangent plane. The value of the TPD are the same as the values of the TPD are at the stationary points of the TPD function when capillary pressure is ignored. However, this approach allows the evaluation of the capillary pressure at all other $\vec{d}$ coordinates of the domain. In this case, it is possible that the Algorithm finds a local minimum at even lower TPD values than at the local minima of the TPD function at constant capillary pressures. Although the TPD criterion guarantees the instability once a negative TPD value is found, it assumes that this phase is unstable at that particular capillary pressure. However, during the phase split calculation, the capillary pressure may change since the compositions and molar volumes will change. As the capillary pressure changes, the TPD value might vary and make the phase stable.

Moreover, the parachor correlation was based on the critical scaling theory which describes equilibrium fluid properties near the critical point. In this case however, the capillary pressure is evaluated at every single $\vec{d}$ coordinate which may significantly deviate from equilibrium phases compositions or volumes. Therefore, it is dangerous to truly consider the variations of the capillary pressure for all the $\vec{d}$ coordinates. Some numerical artifacts may arise such as an apparent instability being detected.

One example of this is provided attached to this report. The html file titled "TPD_d1_d2.html" represents our new way of thinking about stability in $\vec{d}$ space. In that one, we can see one surface with two parallel tangent planes corresponding to the two equilibrium phases. The fact that these are at the equilibrium was verified by a flash calculation. The reference phase in this stability analysis is the blue dot. The stationary point and equilibrium phase corresponds to the green dot. This represents the stability analysis at constant capillary pressure. On this figure, we can see that the reference phase is at the limit of stability. The second file is titled "TPD_dPcap_d1_d2.html". This plot represents the TPD function that Nichita's 2019 algorithm minimizes. In this plot, only one tangent plane is considered to evaluate the stability of a mixture on a single surface. Also, the value of the capillary pressure is calculated at every single coordinate point of the TPD function which changes the shape of the TPD. The reference phase and equilibrium phases are represented by dots following the same coloring scheme as the previous plot. The yellow dot corresponds to the solution given by Nichita's algorithm. On this figure, we can actually see a portion of the curve with negative value of TPD. This causes Nichita's algorithm to incorrectly conclude that the phase is unstable when it is actually stable.

Task 2: Derive a method for updating the composition and molar volume / mole numbers as a combined stability analysis/phase split calculation.

Equilibrium can be posed as the following optimization problem:

$$\min \left(\underline{A}\left(T, \underline{V_1}, \underline{V_2}, \vec{x}_1, \vec{x}_2\right)\right)$$
$$s.t.$$
$$\underline{V_1}\beta_1 + \underline{V_2}\beta_2 = \underline{V_{tot}} = constant$$
$$\vec{x}_1\beta_1 + \vec{x}_2\beta_2 = \vec{z} = constant$$

The proposed method is to update the composition of both phases using one Successive Substitution Iteration (SSI) and a lagged molar volume update. The question is the following: What would be the most efficient and robust way to update the molar volume of the two phases after one SS iteration?

First of all, the TPD minimization problem converges to a stationary point satisfying the following equation:

$$\ln\left(f_i^{trial}\right) - \ln\left(f_i^{ref}\right) = 0, i = 1, \dots, N_c$$

Therefore the SSI equation to update the composition written as

$$K_{i,j} = \frac{\ln\left(P_j \phi_{i,j}\right)}{\ln\left(P_{N_p}\phi_{i,N_p}\right)}$$

Where the phase j would correspond to the converged trial phase from the stability analysis and N_p is the reference phase. This equation would not actually alter the compositions in any way because the fugacities of phase j and phase N_p are already satisfied.

Therefore, the volumes of each phase must be updated before updating the composition of the two phases.

Three solution methods have already been proposed to update molar volumes in a VT flash calculation. The first one was introduced by Mkikyska and Firoozabadi (2010). They proposed to use a bisection method to update the volumes so as to solve the pressure equality relation. The variable to be updated in this bisection is the vapor phase saturation with a range from 0 to 1. The pressure equation is the following:

$$F_P(S_V) = P_V - P_L = 0$$

Nichita (2018 a) criticized this method saying that the range of saturation of 0 to 1 is incorrect because this range might violate the physical constraint on the molar volume which is that it should be greater than the covolume parameter. Nichita points out that in the saturation range

{0,1}there could be up to four asymptotes in the pressure equation for a cubic EOS such as PR EOS. Those asymptotes can be found analytically:

$$\underline{V_V} = \sum_i^N b_i x_{iV} \; ; \; \underline{V_L} = \sum_i^N b_i x_{iL} \; ; \; \underline{V_V} = \left(\sqrt{2} - 1\right) \sum_i^N b_i x_{iV} \; ; \; \underline{V_L} = \left(\sqrt{2} - 1\right) \sum_i^N b_i x_{iL} \; ;$$

Therefore, Nichita redefined the correct saturation range to be $S_V \in \left\{\frac{\sum_i^N b_i x_{iV}}{V_{tot}}, 1 - \frac{\sum_i^N b_i x_{iL}}{V_{tot}}\right\}$. Additionally, Nichita proposes to use Brent's method instead of the bisection method as a faster, equally as robust alternative to bisection to solve the pressure equation in the new saturation domain.

Another approach was proposed by Lu et al. (2019) was to subdivide the saturation range from 0 to 1 in 100 subsections and do a bisection in each region to identify all the roots. After all the roots to the pressure equation have been identified, the correct root is selected if it produces the lowest Helmholtz free energy. They used this method after graphically observing more than one solution to the pressure equation in the saturation range but did not analyze the physical meaning behind those multiple roots. Therefore Nichita's approach might be more robust.

The third method proposed by Nichita (2018 a) involves solving the volume balance at a constant pressure instead of solving the pressure equation. This new equation is the following:

$$F_V(P) = \underline{V_V}(P)\beta_V + \underline{V_L}(P)\beta_L - \underline{V_{spec}} = 0$$

The advantages of this method are that the saturation bounds are enforced implicitly. Moreover, this method only gives a unique solution for P>0 since $\left(\frac{\partial V}{\partial P}\right)_{T,n} < 0 \Rightarrow \left(\frac{\partial F_V}{\partial P}\right)_{T,n} < 0$. However, for the case of VT flash with capillary pressure, this method should be avoided since root selection to determine the volume form a known pressure based on the lowest Gibbs free energy was shown not to be robust (Neshat, 2018).

The method that is proposed here is based on updating the volumes by direct minimization of Helmholtz Free Energy. This method is similar to the one Nichita (2018 b) derived although in our case, the problem is defined with temperature and volume instead of temperature and pressure.

Capillary equilibrium is a minimization problem where the equilibrium phase compositions lie on parallel tangent planes in $\vec{d}$ space. This can only be obtained by minimizing the Helmholtz free energy at constant capillary pressure and updating the capillary pressure in a separate step. Therefore we derive the flash problem by assuming that the capillary pressure is constant. The following proof follows the methodology of Nichita (2018 b).

$$A_r = \frac{A}{RT} = \sum_i^N n_{iV} \ln(f_{iV}) + \sum_i^N n_{iL} \ln(f_{iL}) - \frac{P_L V_L}{RT} - \frac{P_V V_V}{RT} + \frac{\sigma_{LV} A_{LV}}{RT}$$

In component molar density coordinates, the reduced Helmholtz free energy becomes:

$$A'_r = \sum_i^N d_{iV} \ln(f_{iV}) + \sum_i^N d_{iL} \ln(f_{iL}) - \frac{P_L S_L}{RT} - \frac{P_V(1 - S_L)}{RT} + \frac{\sigma_{LV}\alpha_{LV}}{RT}$$

Where α_{LV} is the specific area of the interface.

The gradient of the reduced Helmholtz free energy in n V space is the following expression:

$$g_i = \left(\frac{\partial A_r}{\partial n_{iV}}\right)_{T,n_{j\neq i},V} = \ln(f_{iV}) - \ln(f_{iL}), i = 1, \dots N_c$$

$$g_{N_c+1} = \left(\frac{\partial A_r}{\partial V_V}\right)_{T,\underline{n}} = -\frac{\left(P_V - P_L + P_{cap}\right)}{RT}$$

The Newton iteration is

$$H\overrightarrow{\Delta\xi} = -\vec{g}$$

Where $\overrightarrow{\Delta\xi}$ is defined as the following:

$$(\Delta\xi)_i = \Delta n_{iV}, i = 1, \dots, N_c$$
$$(\Delta\xi)_{N_c+1} = \Delta V_L, i = 1, \dots, N_c$$

Where the hessian is

$$H_{ij} = \frac{\partial^2 A_r}{\partial\xi_i\partial\xi_j} = \frac{\partial g_i}{\partial\xi_j} = \frac{\partial g_j}{\partial\xi_i}$$

The hessian can be decomposed into four blocks:

$$H = \begin{vmatrix} A & \vec{B} \\ \vec{B}^T & D \end{vmatrix}$$

$$A_{ij} = \left(\frac{\partial g_i}{\partial n_j}\right)_{T,n_{k\neq j},V}, i = 1, \dots, N_c; j = 1, \dots, N_c$$

$$B_j = \left(\frac{\partial g_{N_c+1}}{\partial n_j}\right)_{T,n_{k\neq j},V} = \left(\frac{\partial g_j}{\partial V_V}\right)_{T,n_{k\neq j},V}, j = 1, \dots, N_c$$

$$D = \left(\frac{\partial g_{N_c+1}}{\partial V_V}\right)_{T,\underline{n}}$$

We can also split the gradient vector into two parts:

$$\vec{g} = \begin{vmatrix} \vec{g}_n \\ g_V \end{vmatrix} \quad s.t. \, g_{n_i} = g_i, i = 1, \dots, N_c \text{ and } g_V = g_{N_c+1}$$

If the natural logarithms of the K values are to be used instead of the component mole numbers in each phase, then the linear system can be written as

$$\begin{vmatrix} \boldsymbol{A}\boldsymbol{U}^{-1} & \vec{\mathrm{B}} \\ \vec{\mathrm{B}}^T U^{-1} & D \end{vmatrix} \cdot \begin{vmatrix} \overrightarrow{\Delta\ln(\mathrm{K})} \\ \Delta V_V \end{vmatrix} = - \begin{vmatrix} \vec{g}_n \\ g_V \end{vmatrix}$$

Where the matrix **U** is defined as the matrix corresponding to the following change of variable:

$$\overrightarrow{\Delta\ln(\mathrm{K})} = \boldsymbol{U}\overrightarrow{\Delta n_v}$$

$$U_{ij} = \left(\frac{\partial \ln(K_{ij})}{\partial n_{iV}}\right)_{T,n_{j\neq i,V},V_V} = \frac{1}{n_V n_L}\left(\frac{\delta_{ij}}{u_i} - 1\right); u_i = \frac{x_i y_i}{z_i}$$

As pointed out by Mehra et al (1983), the SSI in PT formulation can be obtained by setting the elements on the diagonal of the hessian to 1 and the off-diagonal elements to 0. A similar form may be obtained with the VT formulation by setting **B** to 0 and by setting **A** to be the inverse of **U**. We then obtain the following linear system of equations :

$$\begin{vmatrix} \boldsymbol{I} & \vec{0} \\ \vec{0} & D \end{vmatrix} \cdot \begin{vmatrix} \overrightarrow{\Delta\ln(\mathrm{K})} \\ \Delta V_V \end{vmatrix} = - \begin{vmatrix} \vec{g}_n \\ g_V \end{vmatrix}$$

The set of linear equations at the top is then identical to the SSI used in PT flash. The bottom equation is a newton update of the volume to directly minimize the total Helmholtz Free Energy. The volume update equation which corresponds more naturally to the SSI is then

$$D \, \Delta V_V = -g_V$$

$$D = \left(\frac{\partial g_{N_c+1}}{\partial V_V}\right)_{T,\underline{n}} = \frac{-\left(\frac{\partial P_L}{\partial V_L}\right)_{T,\underline{n}} - \left(\frac{\partial P_V}{\partial V_V}\right)_{T,\underline{n}}}{RT}$$

$$\Delta V_V = -\frac{-(P_V - P_L + P_{cap})}{-\left(\frac{\partial P_L}{\partial V_L}\right)_{T,\underline{n}} - \left(\frac{\partial P_V}{\partial V_V}\right)_{T,\underline{n}}} = -\frac{P_V - P_L + P_{cap}}{\left(\frac{\partial P_L}{\partial V_L}\right)_{T,\underline{n}} + \left(\frac{\partial P_V}{\partial V_V}\right)_{T,\underline{n}}}$$

This lagged update is identical to the following formulation:

$$\min\left(\underline{A}(\underline{V}_1, \underline{V}_2)\right)$$
$$s.t.$$
$$T, \underline{V}_{tot}, \vec{x}_1, \vec{x}_2 \text{ are held constant}$$
$$\underline{V}_1\beta_1 + \underline{V}_2\beta_2 = \underline{V}_{tot}$$

This volume update works together with the SSI more naturally than the bisection method since their combination is a result of the derivation of the algorithm. One advantage of this formulation

compared bisection or Brent's method to solve either the pressure equation is that there is no need to worry about the potential presence of multiple roots. This algorithm only seeks the local solution that is the closest to the previously guessed value.

The main difference between the above formulation and the one derived by Nichita (2018 b) is that his work considers the volume of the vapor and the volume of the liquid as independent variables since his formulation was derived for a specified pressure instead of a specified molar volume. When the pressure is used as the specified variable, the above set of linear equations become the following:

$$\begin{vmatrix} I & 0 \\ 0 & \overrightarrow{D} \end{vmatrix} \cdot \begin{vmatrix} \overrightarrow{\Delta \ln (K)} \\ \overrightarrow{\Delta V} \end{vmatrix} = - \begin{vmatrix} \overrightarrow{g_n} \\ \overrightarrow{g_V} \end{vmatrix}$$

$$g_{V_1} = \frac{P^{spec} - P_V}{RT}$$

$$g_{V_2} = \frac{P^{spec} - P_V}{RT}$$

Nichita claims that the above formulation for SSI is not robust since iterates may go out of the feasible domain and a line search is often required and a descent direction is not guaranteed. No further proof is proposed to support these claims.

Task 3: Do a manual combined stability analysis and phase split calculation.

For this exercise, we take an binary mixture of C1 and C20 at equilibrium and disturb it slightly to put it in the unstable region. We parametrize the flash problem such that the solution is known and lies on a similar TPD curve as the one used in Task 1.

phase index	V	L	Bulk
x1	0.548333	0.054446	0.3
x20	0.451667	0.945554	0.7
beta	0.497187	0.502813	
$\underline{V}$ (ft^3/lbmol)	70.142	11.817	40.815346
P (psia)	170.69	141.41	
d1 (lbmol/ ft3)	0.007817	0.004607	
d20 (lbmol/ ft3)	0.006439	0.080017	

Table 1 - Known solution of flash problem to be solved for a cylinder radius of 10 nm

We will initiate the calculation at the following coordinates in d space.

	Mole fraction	Molar density
C1	0.445827603	0.00629777175
C20	0.554172397	0.00782825300

Table 2 - Table of composition used to initiate flash

The algorithm used is the following:

1. Set k=1, set $x_j{}^k$ to the initial composition.
2. Conduct a Stability Analysis (SA) on the mixture $x_j{}^k$. The non-trivial stationary point is named $x_{j+1}{}^k$
3. Update the volumes of phases j and j+1 using the equation $D \, \Delta V_V = -g_V$
4. Update the K-values of both phases at a fixed volumes by using the SSI equation:
$$\ln(K_i^k) = \ln(\phi_{i,j+1} P_{j+1}) - \ln(\phi_{i,j} P_j)$$
5. If TPD=0 and mole balance and volume balance are satisfied, exit the algorithm. Otherwise, go back to step 2.

The details of each step is described below.

ITERATION 1:
The composition can be found in the table below.

	Mole fraction	Molar density
C1	0.445827603	0.00629777175
C20	0.554172397	0.00782825300

Table 3 - Reference composition at SA iteration 1

Molar volume	70.79132433	ft³/lbmol
P	158.7864868	Psia

Table 4 - Molar volume and pressure of reference composition at SA iteration 1

The TPD at this initial composition is plotted and attached to this report. The file is called "TPD_ITER1.html".
The stationary point obtained corresponds to the following: coordinates:

	Mole fraction	Molar density
C1	0.035563047	0.006219234
C20	0.964436953	0.010045437

Table 5 - Stationary point composition obtained from SA at iteration 1

Molar volume	11.34157472	ft³/lbmol
P	229.1275573	psia
TPD	-8.82E-02	
Pcap	34.81367571	psia

Table 6 - Stationary point molar volume and pressure obtained from SA at iteration 1

After the SS iteration, we get the following:

Liquid	Mole fraction	Molar density
C1	0.053015119	0.004383566
C20	0.946984881	0.078301642

Molar volume	12.09406163	ft³/lbmol
P	100.5356805	psia

Vapor	Mole fraction	Molar density
C1	0.516982776	0.007346812
C20	0.483017224	0.006864129

Molar volume	70.36831802	ft³/lbmol
P	167.152785	psia

Table 7 – Phase properties after SSI at iteration 1

Table 7 – Phase properties after SSI at iteration 1

ITERATION 2:

The composition can be found in the table below.

	Mole fraction	Molar density
C1	0.51698277563	0.00734681161
C20	0.48301722437	0.00686412917

Table 8 - Reference composition at SA iteration 2

Molar volume	70.36831802	ft³/lbmol
P	167.152785	Psia

Table 9 - Molar volume and pressure of reference composition at SA iteration 2

The TPD at this initial composition is plotted and attached to this report. The file is called "TPD_ITER2.html".

The stationary point obtained corresponds to the following: coordinates:

	Mole fraction	Molar density
C1	0.04896940239	0.00421345709
C20	0.95103059761	0.08182919168

Table 10 - Stationary point composition obtained from SA at iteration 2

Molar volume	11.62214337	ft³/lbmol
P	171.7455474	psia
TPD	-3.10E-02	
Pcap	31.4983723	psia

Table 11 - Stationary point molar volume and pressure obtained from SA at iteration 2

After the SS iteration, we get the following:

Liquid	Mole fraction	Molar density
C1	0.055093075	0.004605456
C20	0.944906925	0.07898865

Molar volume	11.96256581	ft³/lbmol
P	120.1039566	psia

Vapor	Mole fraction	Molar density
C1	0.543422749	0.007743343
C20	0.456577251	0.006505864

Molar volume	70.17934211	ft³/lbmol
P	170.140766	psia

Table 12 – Phase properties after SSI at iteration 2

ITERATION 3:
The composition can be found in the table below.

	Mole fraction	Molar density
C1	0.54342274907	0.00774334345
C20	0.45657725093	0.00650586394

Table 13 - Reference composition at SA iteration 3

Molar volume	70.17934211	ft³/lbmol
P	170.140766	Psia

Table 14 - Molar volume and pressure of reference composition at SA iteration 3

The TPD at this initial composition is plotted and attached to this report. The file is called "TPD_ITER3.html".

The stationary point obtained corresponds to the following: coordinates:

	Mole fraction	Molar density
C1	0.05351848576	0.00454236992
C20	0.94648151424	0.08033241407

Table 15 - Stationary point composition obtained from SA at iteration 3

Molar volume	11.78206239	ft³/lbmol
P	146.3811792	psia
TPD	-5.15E-03	
Pcap	29.66684761	psia

Table 16 - Stationary point molar volume and pressure obtained from SA at iteration 3

After the SS iteration, we get the following:

Liquid	Mole fraction	Molar density
C1	0.054670701	0.004614881
C20	0.945329299	0.079797442

Molar volume	11.84661159	ft³/lbmol
P	136.935119	psia

Vapor	Mole fraction	Molar density
C1	0.548099975	0.007813961
C20	0.451900025	0.006442491

Molar volume	70.14368138	ft³/lbmol
P	170.6636156	psia

Table 17 – Phase properties after SSI at iteration 3

ITERATION 4:

The composition can be found in the table below.

	Mole fraction	Molar density
C1	0.54809997486	0.00781396077
C20	0.45190002514	0.00644249084

Table 18 - Reference composition at SA iteration 4

Molar volume	70.14368138	ft^3/lbmol
P	170.6636156	Psia

Table 19 - Molar volume and pressure of reference composition at SA iteration 4

The TPD at this initial composition is plotted and attached to this report. The file is called "TPD_ITER4.html".
The stationary point obtained corresponds to the following: coordinates:

	Mole fraction	Molar density
C1	0.05440052579	0.00460425778
C20	0.94559947421	0.08003201566

Table 20 - Stationary point composition obtained from SA at iteration 4

Molar volume	11.81526501	ft^3/lbmol
P	141.6517734	psia
TPD	-2.49E-04	
Pcap	29.29643607	psia

Table 21 - Stationary point molar volume and pressure obtained from SA at iteration 4

After the SS iteration, we get the following:

Liquid	Mole fraction	Molar density
C1	0.054457656	0.004607843
C20	0.945542344	0.080005484

Molar volume	11.8184691	ft^3/lbmol
P	141.1849251	psia

Vapor	Mole fraction	Molar density
C1	0.548329608	0.007817432
C20	0.451670392	0.006439379

Molar volume	70.14191273	ft^3/lbmol
P	170.689243	psia

Table 22 – Phase properties after SSI at iteration 4

ITERATION 5:
The composition can be found in the table below.

	Mole fraction	Molar density
C1	0.54832960830	0.00781743165
C20	0.45167039170	0.00643937945

Table 23 - Reference composition at SA iteration 5

Molar volume	70.14191273	ft^3/lbmol
P	170.689243	Psia

Table 24 - Molar volume and pressure of reference composition at SA iteration 5

The TPD at this initial composition is plotted and attached to this report. The file is called "TPD_ITER5.html".
The stationary point obtained corresponds to the following: coordinates:

	Mole fraction	Molar density
C1	0.05444453117	0.00460732900
C20	0.94555546883	0.08001694631

Table 25 - Stationary point composition obtained from SA at iteration 5

Molar volume	11.81694019	ft^3/lbmol
P	141.4176721	psia
TPD	-5.49E-06	
Pcap	29.27784568	psia

Table 26 - Stationary point molar volume and pressure obtained from SA at iteration 5

After the SS iteration, we get the following:

Liquid	Mole fraction	Molar density
C1	0.054445793	0.004607408
C20	0.945554207	0.08001636

Molar volume	11.81701094	ft^3/lbmol
P	141.4073654	psia

Vapor	Mole fraction	Molar density
C1	0.548334676	0.007817508
C20	0.451665324	0.006439311

Molar volume	70.14187368	ft^3/lbmol
P	170.6898085	psia

Table 27 – Phase properties after SSI at iteration 5

ITERATION 6:

The composition can be found in the table below.

	Mole fraction	Molar density
C1	0.54833467629	0.00781750825
C20	0.45166532371	0.00643931079

Table 28 - Reference composition at SA iteration 6

Molar volume	70.14187368	ft³/lbmol
P	170.6898085	Psia

Table 29 - Molar volume and pressure of reference composition at SA iteration 6

The stationary point obtained corresponds to the following: coordinates:

	Mole fraction	Molar density
C1	0.05444550313	0.00460739681
C20	0.94555449687	0.08001661339

Table 30 - Stationary point composition obtained from SA at iteration 6

Molar volume	11.81697721	ft³/lbmol
P	141.4125035	psia
TPD	-1.14E-07	
Pcap	29.27743496	psia

Table 31 - Stationary point molar volume and pressure obtained from SA at iteration 6

After the SS iteration, we get the following:

Liquid		
	Mole fraction	Molar density
C1	0.054445529	0.004607398
C20	0.945554471	0.080016601

Molar volume	11.81697868	ft³/lbmol
P	141.4122901	psia

Vapor		
	Mole fraction	Molar density
C1	0.548334781	0.00781751
C20	0.451665219	0.006439309

Molar volume	70.14187287	ft³/lbmol
P	170.6914839	psia

Table 32 – Phase properties after SSI at iteration 6

ITERATION 7:

The composition can be found in the table below.

	Mole fraction	Molar density
C1	0.54833478123	0.00781750984
C20	0.45166521877	0.00643930936

Table 33 - Reference composition at SA iteration 7

Molar volume	70.14187287	ft^3/lbmol
P	170.6914839	Psia

Table 34 - Molar volume and pressure of reference composition at SA iteration 7

The stationary point obtained corresponds to the following: coordinates:

	Mole fraction	Molar density
C1	0.05444552326	0.00460739822
C20	0.94555447674	0.08001660649

Table 35 - Stationary point composition obtained from SA at iteration 7

Molar volume	11.81697798	ft^3/lbmol
P	141.4123965	psia
TPD	-2.35E-09	
Pcap	29.27742645	psia

Table 36 - Stationary point molar volume and pressure obtained from SA at iteration 7

After the SS iteration, we get the following:

Liquid

	Mole fraction	Molar density
C1	0.054445524	0.004607398
C20	0.945554476	0.080016606

Molar volume	11.81697801	ft^3/lbmol
P	141.4123921	psia

Vapor

	Mole fraction	Molar density
C1	0.548334783	0.00781751
C20	0.451665217	0.006439309

Molar volume	70.14187286	ft^3/lbmol
P	170.6898205	psia

Table 37 – Phase properties after SSI at iteration 7

ITERATION 8:

The composition can be found in the table below.

	Mole fraction	Molar density
C1	0.54833478340	0.00781750987
C20	0.45166521660	0.00643930933

Table 38 - Reference composition at SA iteration 8

Molar volume	70.14187286	ft³/lbmol
P	170.6898205	Psia

Table 39 - Molar volume and pressure of reference composition at SA iteration 8

The stationary point obtained corresponds to the following: coordinates:

	Mole fraction	Molar density
C1	0.05444552367	0.00460739825
C20	0.94555447633	0.08001660635

Table 40 - Stationary point composition obtained from SA at iteration 8

Molar volume	11.81697799	ft³/lbmol
P	141.4123943	psia
TPD	-4.85E-11	
Pcap	29.27742628	psia

Table 41 - Stationary point molar volume and pressure obtained from SA at iteration 8

After the SS iteration, we get the following:

Liquid

	Mole fraction	Molar density
C1	0.054445524	0.004607398
C20	0.945554476	0.080016606

Molar volume	11.81697799	ft³/lbmol
P	141.4123942	psia

Vapor

	Mole fraction	Molar density
C1	0.548334783	0.00781751
C20	0.451665217	0.006439309

| Molar volume	70.14187286	ft³/lbmol
P	170.6898205	psia

Table 42 – Phase properties after SSI at iteration 8

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A summary of the compositions at the end of all the iterations is presented below :

	ITER0	ITER1	ITER2	ITER3	ITER4	ITER5	ITER6	ITER7	ITER8
X_{1V}	0.44583	0.51698	0.54342	0.54810	0.54833	0.54833	0.54833	0.54833	0.54833
X_{2V}	0.55417	0.48302	0.45658	0.45190	0.45167	0.45167	0.45167	0.45167	0.45167
X_{1L}		0.05302	0.05509	0.05467	0.05446	0.05445	0.05445	0.05445	0.05445
X_{2L}		0.94698	0.94491	0.94533	0.94554	0.94555	0.94555	0.94555	0.94555
V_V	70.79132	70.36832	70.17934	70.14368	70.14191	70.14187	70.14187	70.14187	70.14187
V_L		12.09406	11.96257	11.84661	11.81847	11.81701	11.81698	11.81698	11.81698
P_V	158.78649	167.15278	170.14077	170.66362	170.68924	170.68981	170.69148	170.68982	170.68982
P_L		100.53568	120.10396	136.93512	141.18493	141.40737	141.41229	141.41239	141.41239
P_{cap}		34.81368	31.49837	29.66685	29.29644	29.27785	29.27743	29.27743	29.27743
TPD		$-8.82\ 10^{-2}$	$-3.10\ 10^{-2}$	$-5.15\ 10^{-3}$	$-2.49\ 10^{-4}$	$-5.49\ 10^{-6}$	$-1.14\ 10^{-7}$	$-2.35\ 10^{-9}$	$-4.85\ 10^{-11}$

The compositions, molar volumes, and pressures above are the properties of the two phases at iteration after the SS iteration and volume update.

The following is a plot of TPD values with each iteration.
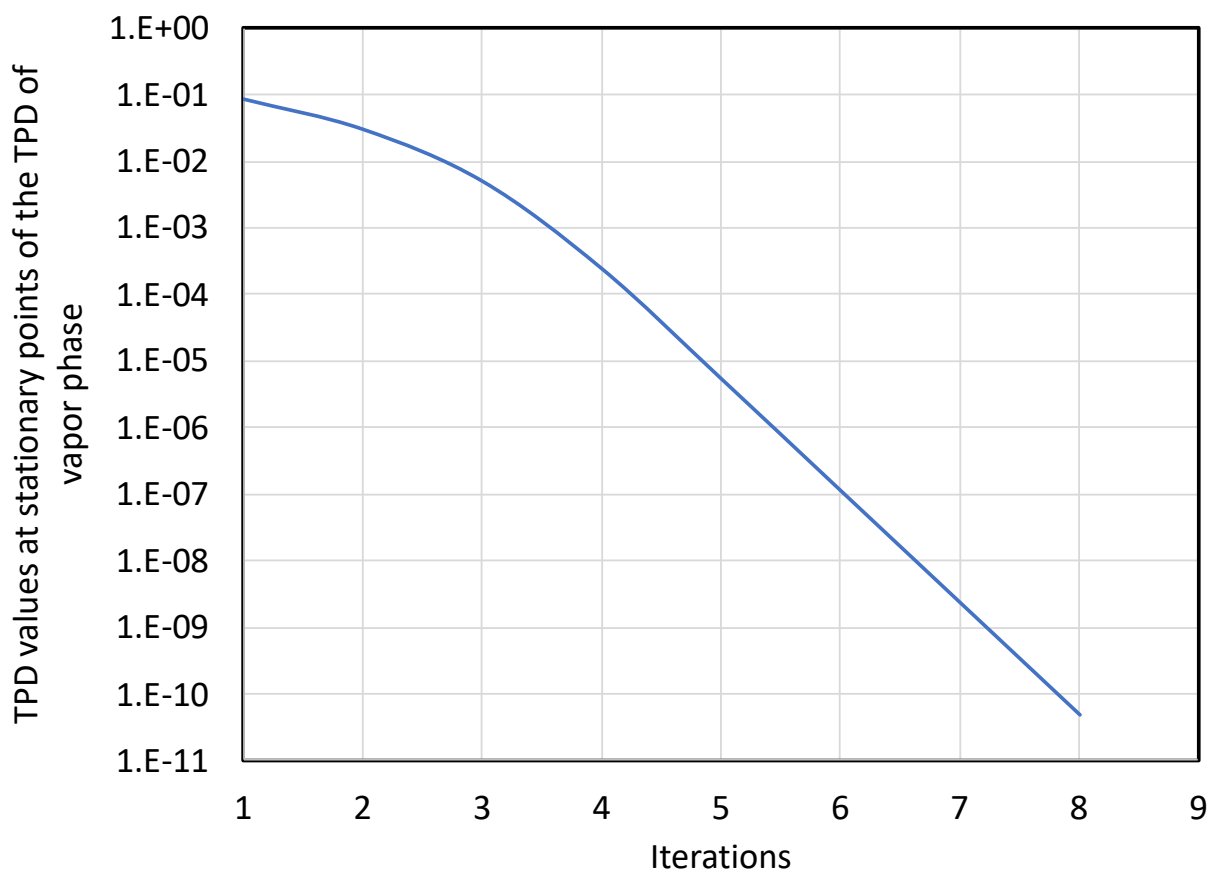
Date of submission: 06/10/2019

Task 4: Describe and implement the stability analysis algorithm in component molar density to a saturation dependent capillary pressure model.

$$P_{c,og}(S_o, S_{wc}, S_g) = \sigma_{og} \sqrt{\frac{\phi}{k} \left(\frac{b_o}{(S_o + S_{wc})^{a_o}} + \frac{b_g}{S_g^{a_g}} \right)}$$

The following algorithm is proposed (assuming that the mixed-wet):

1. Launch a SA using the block composition and molar volume or the pressure of such block
2. If no stationary point is found, then exit the subroutine, the fluid is stable and forms a single phase. If a stationary point, identify the type of the stationary point using the difference in Gibbs free energy with the reference point. The stationary point is vapor-like if its Gibbs free energy is higher than the reference phase. Otherwise, it is considered a liquid-like phase.

Case 1: The stationary point is vapor-like

3. Compute the TPD at the stationary point by using the capillary pressure at minimum oil saturation:
$$TPD_{SP} = P_{cap}(S_{o,min}) + P_o - P_g$$
$S_{o,min}$ needs to be taken slightly above the residual saturation. This is done in order to mitigate the appearance of near infinite numbers near residual saturations. 0.0001 is used in the current implementation.
4. If the TPD is positive and the mixture forms a single phase at the specified conditions. If the TPD is negative, the mixture splits in two phases at equilibrium.

Case 2: The stationary point is liquid-like

1. Compute the TPD at the stationary point by using the capillary pressure at maximum oil saturation:
$$TPD_{SP} = P_{cap}(S_{o,max}) + P_o - P_g$$
$S_{o,max}$ needs to be taken slightly below the residual saturation. This is done in order to mitigate the appearance of near infinite numbers near residual saturations. 0.9999-S_{wc} is used in the current implementation.
2. If the TPD is positive and the mixture forms a single phase at the specified conditions. If the TPD is negative, the mixture splits in two phases at equilibrium.

This algorithm was tested on the C1-C20 50:50 mixture at the bubble point at 800°F. The following are the parameters used for this mixture:

Parachor Exponent	Swc	ø	K (mD)	bo	bg	ao	ag
3.88	0.1	0.2	5. 10^{-3}	4.3 10^{-3}	0.0	2.8	2.2

Except for the permeability, all capillary pressure parameters were taken from Sajjad' ATCE paper.

When capillary pressure is not taken into account, the bubble point is 1384.6016 psia. The bubble point can be found at 1312.8056 psia, with a molar volume of 8.098714105 ft^3/lbmol. The capillary pressure at convergence is about 11.3 psia. This value was found by using a negative flash calculation subroutine.

However, the stability test indicated that the phase boundary was rather between 8.11 and 8.12 ft^3/lbmol. This corresponds to a bubble point pressure between 1312.17302110659 and 1309.30301454956 psia.

For the moment, it is unclear whether this disagreement is proof that the algorithm gives an incorrect answer or whether the negative flash routine is not converging to the correct solution to the flash problem. Some unusual apparent discontinuities were noticed with the negative flash results at convergence.

This algorithm was next tested on the C1-C20 50:50 mixture at the dew point at 800˚F. The following are the parameters used for this mixture:

Parachor Exponent	Swc	ø	K (mD)	bo	bg	ao	ag
3.88	0.1	0.2	$1.0\ 10^{-6}$	$4.3\ 10^{-3}$	0.0	2.8	2.2

When capillary pressure is not taken into account, the bubble point is 158.5039 psia. The dew point can be found at 155.7264 psia, with a molar volume of 75.4469 ft^3/lbmol. The capillary pressure at convergence is about 9.5 psia. This value was found by using a negative flash calculation subroutine.

The stability test algorithm agreed that the phase boundary was between 75.5 and 75.4 ft^3/lbmol.

Biography

R.K. Mehra, R.A. Heidemann, K. Aziz, An accelerated successive substitution algorithm, Can. J. Chem. Eng. 61 (1983) 590-596.

Mikyška, J., & Firoozabadi, A. (2011). A new thermodynamic function for phase-splitting at constant temperature, moles, and volume. AIChE Journal, 57(7), 1897-1904.

Nichita, D. V. (2019). Volume-based phase stability analysis including capillary pressure. Fluid Phase Equilibria.

Nichita, D. V. (2018a). New unconstrained minimization methods for robust flash calculations at temperature, volume and moles specifications. Fluid Phase Equilibria, 466, 31-47.

Nichita, D. V. (2018b). A volume-based approach to phase equilibrium calculations at pressure and temperature specifications. Fluid Phase Equilibria, 461, 70-83.

Neshat, S. S., Okuno, R., & Pope, G. A. (2018). A rigorous solution to the problem of phase behavior in unconventional formations with high capillary pressure. SPE Journal, 23(04), 1-438.