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Postgraduate Program in Petroleum Engineering

Critical evaluation higher asphaltene onset point (h-AOP) and lower asphaltene onset point (l-AOP) and comparison with various thermodynamic models predictions

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Abstract

Asphaltene deposition is a challenging problem in the oil industry in many regions around the world. Due to the tendency of this petroleum fraction it precipitates and deposits in the wellbore, near wellbore region, and surface facilities, as a result of changes in pressure, temperature, and composition. Prediction of asphaltene phase behavior is important in order to avoid possible problems that can occur with their deposition. The aim of this thesis is to compare predictions of asphaltene phase behavior of two thermodynamic models, PC-SAFT and CPA. For such purpose commercial software HydraFLASH and Multiflash were used. The differences between models' prediction of asphaltene phase behavior was investigated for both lower and upper asphaltene phase boundary.

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1. Introduction

Asphaltenes represent the heaviest fractions of crude oil. They tend to precipitate due to changes in pressure, temperature, and oil composition, which makes them challenging problem in petroleum industry. As the oil industry moves toward deeper reservoirs and relies more on integrated production systems, the probability of encountering asphaltene precipitation problems and the costs associated with their existence will only increase. For instance, in oil fields in the Gulf of Mexico, the average expenses associated with the asphaltene deposition problem is around US $70 million per well when well shut-in is required (González 2015). Asphaltene precipitation is not limited to low temperatures, hence precipitation may occur in the reservoir, in the production well, during pipeline transportation, and in process plants. The deposition of asphaltenes may cause problems by clogging the wellbore, damaging the formation, it can lead to decrease in the production, cause shutting of wells, make damage on the tools, so extra money needs to be invested to solve the problem, or even wells can be lost.

The most common definition of asphaltenes in the literature is definition by solubility stating that asphaltenes are the constituents of an oil mixture that, at room temperature, are practically insoluble in n-pentane and n-heptane, but soluble in benzene and toluene. (Pederson et. al, 2015). This definition based on solubility makes the asphaltenes the least soluble fraction of petroleum and indicates that the asphaltenes can be precipitated with addition of alkenes to the crude oil.

Asphalt is a term used to describe the combination of asphaltenes and resins. Resins can be defined as the fraction of crude oil that is soluble in n-heptane (Pederson et. al, 2015), toluene, and benzene at room temperature. Resins have a strong tendency to associate with asphaltenes due to their opposite charge. This means that if asphaltenes and resins are placed in an electrical field, they will migrate to the oppositely charged electrode. The most common theory for describing the asphaltene-resin interaction assumes that asphaltene micelles (aggregates) exist in the oil as solid particles in colloidal suspension and that resins are absorbed on their surface (Tarek Ahmet, 2016). Resins act as a protective layer and stabilize asphaltenes. This reduces the aggregation of asphaltenes, which determines to a large extent their solubility in crude oil. Because asphaltene particles are stabilized by this “protective shield” of resins, any action of a chemical, electrical, or mechanical nature that removes the resin protective layer might lead to flocculation and precipitation of asphaltenes.

The term asphaltenes may cover a range of different components. Asphaltenes consist of the heaviest fractions of crude oil, primarily of carbon, hydrogen, nitrogen, oxygen, and sulfur, as well as trace amounts of vanadium, nickel, and other metals. One molecule of asphaltene consists of a number of polyaromatic clusters with side aliphatic chains and other functional groups.

When compared with other crude oil components, asphaltenes are the heaviest fraction of a distribution in terms of molecular weight as well as aromaticity. Measurements of molecular diffusion for asphaltenes using the time-resolved fluorescence depolarization technique have indicated that asphaltene molecules are monomeric with average molecular weight of 750 g/mol and a range of 500–1000 g/mol (Groenzin and Mullins 1999, 2000). These values for asphaltene molecular weight have been confirmed by other techniques used to measure asphaltene molecular diffusion, such as Taylor dispersion (Wargadalam et al. 2002), nuclear magnetic resonance (Freed 2007), and fluorescence correla et al. tion spectroscopy (Schneider 2007).

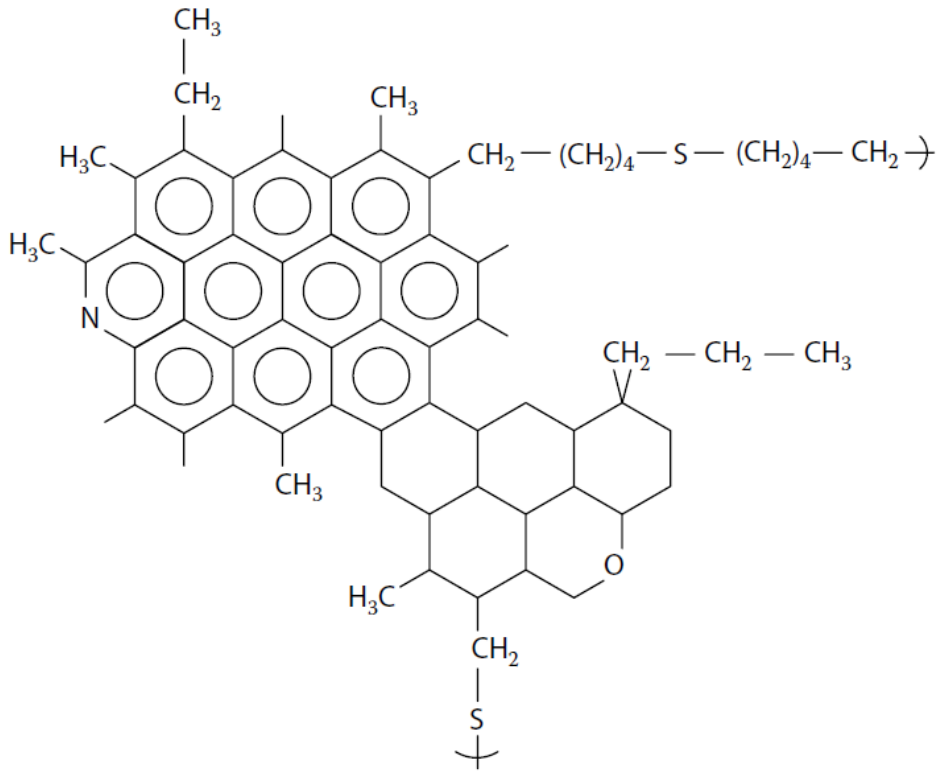


Figure 1. Typical structure of asphaltene molecule

2. Precipitation of Asphaltenes

As stated before, asphaltenes may deposit at any stage of oil exploitation and cause serious problems. Precipitation of asphaltenes occur with changes in temperature, pressure, or composition and deposition problem has been observed in all stages of oil production and processing, in near wellbore formations, production tubing, surface facilities, and refinery units. The amount of asphaltenes in oil can be determined by solvent precipitation tests, but whether asphaltenes may precipitate and cause problems depend on whether they will reach instability during production and transportation of oil. Therefore, knowing the range of temperatures and pressures where asphaltenes may occur presents greater technical challenge than knowing the amount of asphaltenes present in oil (Tarek Ahmed, 2016).

The process of precipitation of asphaltenes with change of conditions was looked as irreversible for many years. In other words, it was believed that asphaltenes that once precipitated cannot go back to solution with oil they originated form. This theory represents asphaltenes as aggregates dissolved in an oil mixture, only staying in solution because of an outer protective layer consisting of resins. If the resin protective layer was removed the asphaltenes form even larger aggregates that would be insoluble, because it would be impossible to regenerate the protective resin layer. The understanding of asphaltene precipitation as a nonreversible process was based on experimental observations of asphaltene precipitation tests by titration where large quantities of either n-pentane or n-heptane were added to stabilized. This technique precipitates asphaltenes in almost pure form, and the cohesion between the individual asphaltene molecules

may be so high that it becomes almost impossible to dissolve the asphaltenes again. (Pederson et. al, 2015)

As opposed to these types of experiments, experimental studies of oils precipitating asphaltenes at reservoir conditions (e.g., Angulo et al. 1995; Jamaluddin et al. 2000 and 2002; Hustad et al. 2014) suggest that asphaltenes may precipitate and dissolve again as is the case with an "ordinary" equilibrium phase (Pederson et. al, 2015). Asphaltenes occur in brief window of pressure and temperature conditions. For exploitation of oil, this range of conditions where asphaltenes occur is very important, hence during production knowing this information can help avoid huge problems.

In precipitation process, solubility of asphaltenes plays a big role. For a constant composition the solubility of asphaltenes decreases with decreasing the pressure. Above bubble point, composition of oil does not change with change of pressure, and if the reservoir temperature constant, only pressure changes will affect asphaltene solubility in oil. As the precipitation of asphaltenes is reversible process (Tarek Ahmed, 2016), the highest asphaltene precipitation is right at the bubble point (see Figure 2). Hence, to quantify the maximum amount of asphaltenes that may precipitate during production, a filtration test is conducted at the bubble-point pressure in a high-pressure filtration apparatus.

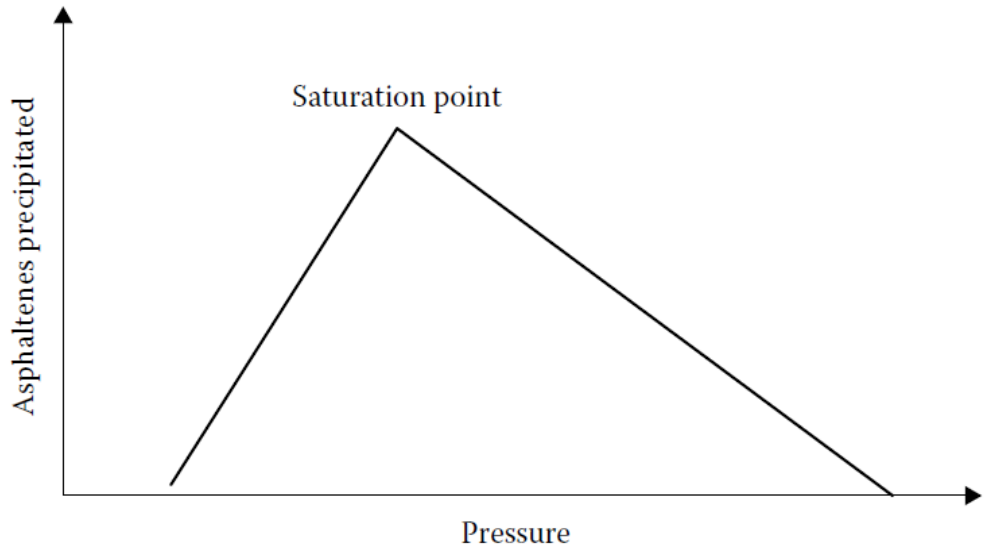


Figure 2 - Amount of asphaltenes precipitated with change in pressure (Pederson et. al, 2015)

The precipitation of asphaltenes can occur during primary depletion of highly undersaturated reservoirs or gas injection for improved oil recovery. The precipitation of asphaltenes from crude oil is a process bounded by pressure and temperature conditions, as shown in Figure 3. The terms upper and lower asphaltene phase boundaries are used to define boundaries for the region of conditions at PT-diagram whereat asphaltene phase are stable. When the precipitation process is observed the upper asphaltene onset pressure represent the pressure at which asphaltenes start coming out of the solution at certain temperature. As pressure decreases more asphaltenes will come out of the solution, and as mentioned before, the highest amount of asphaltenes will come out of solution at the bubble point. Below bubble point asphaltenes will

start coming back to solution and the pressure at which the last asphaltene goes to the solution of oil is called the lower asphaltene onset pressure. (Pederson et. al, 2015)

The reason why asphaltenes will start coming out of the solution on pressures above the bubble point when pressure decreases is because with decrease of the pressure the solubility of asphaltenes in the oil will also decreases.

When the pressure is lowered below bubble point, some gas will come out of solution and change the composition of oil in matter. When gas comes out of the solution the content of n-alkanes decreases in the system hence solubility of asphaltene in oil composition with less n-alkanes will increase. Therefore, asphaltenes will start coming back to the solution and with further pressure decrease asphaltene will continue dissolving in the oil and eventually disappear, at asphaltene lower onset pressure.

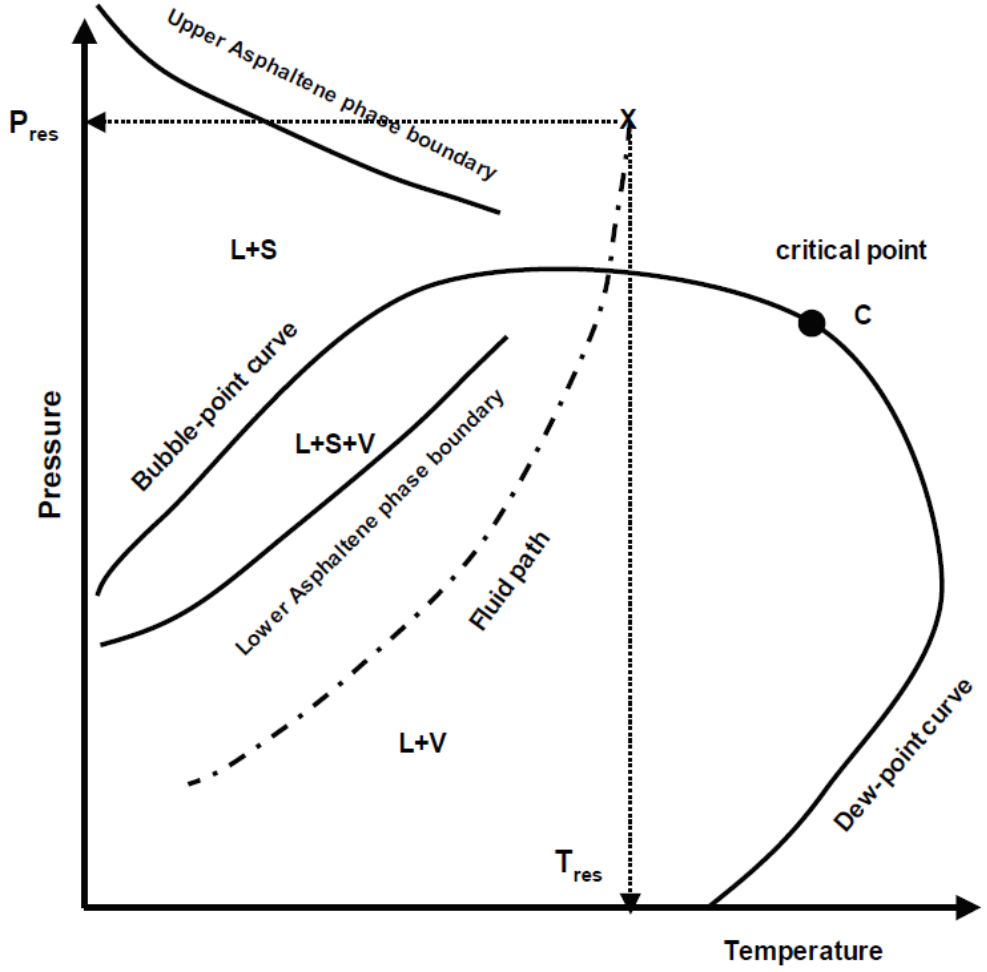


Figure 3 - Asphaltene phase behavior (Tarek Ahmed, 2016)

When the reservoir pressure is above the saturation pressure, the precipitation depends only on the pressure changes, while below the saturation pressure both pressure and composition affect the precipitation behavior., because below bubble point gas starts coming out of solution and changes the composition of oil. The asphaltene deposition envelope of oil is a very useful

tool for evaluating the potential and severity of asphaltene problems. The asphaltene phase boundary shows the fluid path that must be followed during reservoir oil-recovery processes to avoid or minimize asphaltene problems. If possible, the oil should be maintained outside or as far away from the center of the asphaltene phase boundary as possible. (Tarek Ahmed, 2016)

Besides the changes in pressure, gas injection may also trigger asphaltenes to come out of solution. Gas components (N2, CO2, CH4, C2H6, etc.) are bad solvents for the asphaltenes, hence asphaltenes will come out of solution faster when gas is injected in oil, then if it was not injected. The pressure span with asphaltene precipitation widens with an increasing amount of gas added. This means that in oil with more light components upper AOP would be higher and lower AOP would be much lower than in very heavier oil with less light components.

The density of hydrocarbon constituents of the same molecular weight increases in the order paraffins → naphthenes → aromatics (Pederson et. al, 2015). Therefore, asphaltenes have bigger chance to precipitate from a fluid of low density (dominated by paraffins) than from a fluid of high density (dominated by aromatics). This is presented in de Boer plot shown in Figure 4. A reservoir fluid with high asphaltene content is also likely to have a high content of low-molecular-weight aromatics. Since aromatics are good solvents for asphaltenes then, even though fluid has high asphaltene content, no precipitation will take place (Pederson et. al, 2015).

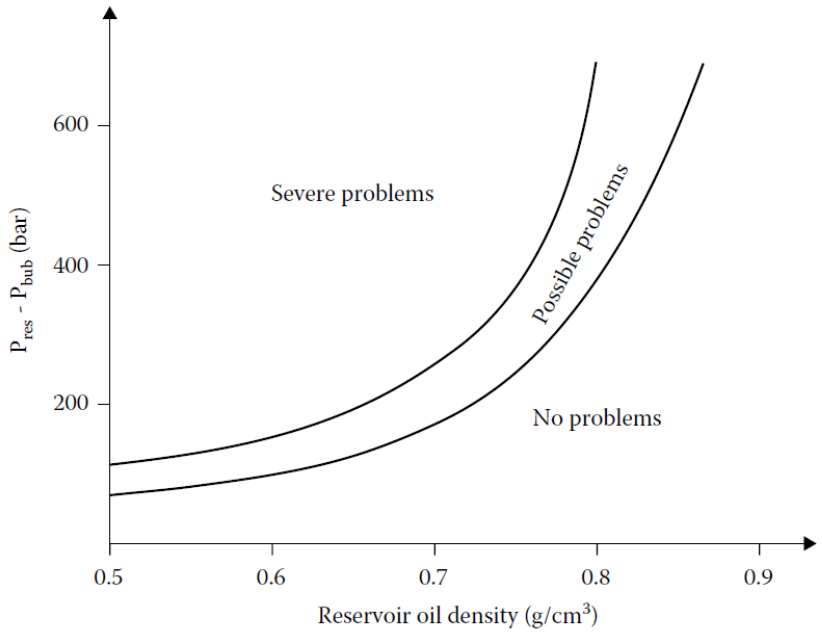


Figure 4 - De Boar Plot (Pederson et. al, 2015)

3. Asphaltene Models

In the literature there is several thermodynamical models describing asphaltene precipitation process. They all resulted from different understanding of asphaltene precipitation mechanism and its complexity. Regardless of the formulation, the goal of these models is to describe the functional dependence of fluid behavior on changes of independent variables, such as temperature, volume and mole number.

According to the mechanism by which asphaltenes are assumed to exist in solution and the factor of solubility, asphaltene precipitation models are classified into following two groups:

1. Micellar models, in which asphaltenes are assumed to be micelles, existing in polar-polar interactions with resins that stabilize them. As described previously, according to this model, if concentration of resins becomes too low compared to asphaltenes, then asphaltenes will precipitate
2. Solubility models, according to which asphaltenes are soluble, partially or fully, in the oil. Asphaltene behavior is dominated by weak Van der Waals interaction, instead of polar interactions.

3.1. Solubility models: EoS

3.1.1. PC-SAFT EoS

PC-SAFT stands for Perturbed Chain Statistical Association Fluid Theory. The model has been developed based on work of Chapman et al. (1988, 1990). The framework of PC-SAFT, molecules are assumed to be chains of freely jointed spherical segments exhibiting attractive forces among each other. The mode development is based on perturbation theories. The basic idea of a perturbation theory is to divide the interactions of molecules into a repulsive part and a contribution due to the attractive part of the potential. The PC-SAFT equation of state requires the specification of three physical parameters: σ, the diameter of each molecular segment, m, the number of segments in the molecule, and ε/k, the interaction energy (van der Waals attraction) between each molecular segment. PC-SAFT model is written in terms of Helmholtz energy with temperature, volume and mole number as independent variables. (Vargas, F., Tavakkoli, M. 2018)

The SAFT EOS family shares the same fundamental form of the EOS:

$$\frac{A^{res}(T,V,n)}{nRT} = \hat{a}^{res} + \hat{a}^{ref} + \hat{a}^{pert}$$

Where A^{res} is the residual Helmholtz energy, $\hat{a}^{\text{res}}$ is the reduced residual molar Helmholtz energy, $\hat{a}^{\text{ref}}$ and $\hat{a}^{\text{pert}}$ are the reference and perturbation contributions, respectively. For PC-SAFT, the reference and perturbation terms are given, respectively, as:

$$\hat{a}^{ref} = \hat{a}^{hc} = \hat{a}^{hs} + \hat{a}^{chain}$$

$$\hat{a}^{pert} = \hat{a}^{disp} + \hat{a}^{assoc}$$

Where $\hat{a}^{hs}$is the hard sphere term, $\hat{a}^{chain}$is chain term, $\hat{a}^{hc}$is hard chain term and it is summation of the hard sphere and chain term. $\hat{a}^{pert}$is perturbation term and it must include all physical forces that are not described by reference fluid. $\hat{a}^{disp}$is dispersion term. For strongly polar fluids dispertion term is not enough to describe phase behavior and in addition association term is used $\hat{a}^{assoc}$.

3.1.2. CPA EoS

The Cubic-Plus-Association (CPA) EOS is, as the name suggests, a combination of the classical cubic EOS and Chapman's association term originally developed for SAFT. In terms of the reduced residual Helmholtz, CPA is given as a physical contribution (cubic EOS) and chemical contribution (association):

$$\hat{a}^{res} = \hat{a}^{SRK} + \hat{a}^{assoc}$$

Unfortunately, the addition of the association term means that CPA is no longer cubic in volume like the classical cubics, so the numerical efficiency that makes the cubics attractive is lost. Additionally, there are five tuning parameters for CPA, which are fit to liquid density and vapor pressure data (like PC-SAFT), instead of the three parameters for cubics fit to the critical point. Thus, CPA improves dramatically on the liquid-volume predictions produced by the cubics, partly because of a retuning of the model parameters and partly because of the additional association term and more fitting parameters. (Vargas, F., Tavakkoli, M. 2018).

4. Material and Methods

Predicting the behavior of asphaltenes due to changes in pressure and temperature is very important in order to avoid possible problems caused by their deposition. Thermodynamic models are used for predicting asphaltene phase boundaries.

In this study performance of two thermodynamic models, PC-SAFT and CPA, is investigated. For this purpose, two software were used: HydraFLASH and Multiflash. For calculating upper and lower asphaltene phase boundary following data is required: composition of oil, SARA analysis and PVT data of crude oil, together with experimental data of asphaltene onset pressure. Finding publicly available data sets that contained all necessary information was demanding job. The calculations of asphaltene phase boundary is not possible without defined composition of fluid and SARA analysis. In most scientific papers data for SARA analysis is not reported, hence this data was not useful for research. In total 22 oil compositions with SARA analysis, PV data and AOP were collected. First step in creating a model is defining a fluid composition. Crude oils contain thousands of components with vastly different chemical structures. Obtaining the concentrations for all these components experimentally is not feasible, and even if it could be done, applying an EoS to such a system would be phase behavior of a crude oil, the crude oil must be characterized into a reasonable number of pseudo-components. The process of defining a set of pseudo-components along with their concentrations and EoS parameters is called *characterization*. For asphaltene characterization SARA analysis is necessary. Besides SARA analysis, data for oil density, GOR, and molecular weight for flashed oil and gas are required as well. If flashed data was not reported in the papers it was necessary to run flash calculations in software as well in order to obtain information for stabilized oil density and molecular weights, as well as for GOR if needed.

In order to calculate asphaltene onset pressure, upper and lower, thermodynamical model must be tuned with experimental data. Calculating EoS parameters, that is, a_i, b_i, and α_i, requires component properties such as Tc, pc, and ω. These properties generally are well-defined for pure components; however, determining these properties for the heavy fractions and lumped components rely on empirical correlations and the use of mixing rules. Tuning an equation of state refers to adjusting the parameters of the selected EoS to achieve a satisfactory match between the laboratory fluid PVT data and EoS results. The experimental data used should be closely relevant to the reservoir fluid and other recovery processes implemented in the field. (Tarek Ahmed, 2016)

In most datasets used in this study, only experimental data for upper onset asphaltene pressure was reported. Only several datasets had lower asphaltenes onset pressure reported. After tuning the model parameters with experimental data asphaltene phase boundary must be calculated. This is the final step in asphaltene phase behavior modelling.

5. Results and discussion

The investigation of software performance was divided in two parts: investigation of performance in predicting upper asphaltene phase boundary and investigation of performance in predicting lower asphaltene phase boundary. In total 50 models were made for calculating upper asphaltene onset boundary and 9 for calculating lower asphaltene phase boundary. Our of 50 models created for upper AOP 7 were unsuccessfully ran because of incorrect data that was reported in papers and they were not taken into account. In 44 models upper AOP was experimental measured with depressurization, and in 6 AOP was measured with gas injection. Out of 9 models created for lower AOP 3 were unsuccessfully ran because of incorrect data. Lower AOP was measured with depressurization and no gas injection experiments were found in publicly available literature. In most of the cases both software performed satisfactorily, in terms of tuning the model parameters and predicting the asphaltene phase behavior. Although both performances were good, few differences in predictions were found and they will be discussed in following chapter, without final judgement which software performed better.

5.1. Asphaltene Phase Boundary

One of the first bold difference that one may encounter when comparing PC-SAFT and CPA models in HydraFLASH and Multiflash software is that, in the most cases, these two thermodynamic models do not give the same asphaltene phase boundary. It seems that PC-SAFT gives exponential relationship between temperature and asphaltene onset pressure when calculating asphaltene boundaries, while CPA model gives parabolic shape of asphaltene phase boundaries. Hence, in this section, only the difference between models will be discussed, from physical point of view, without the final judgement which model performed better in the terms of asphaltene phase envelope shape.

5.1.1. Case 1

Case 1 is an oil for which AOP was measured with gas injection (Jamaluddin et. al, 2000). Experimental asphaltene onset pressure for the Fluid 2b15 composition (see table 1) Oil composition was mixed with 15% of gas and asphaltene onset pressure was measured on temperature of 255 °F. Experimental measurement of asphaltene onset pressure is presented in Table 2. Both CPA and PC-SAFT models were tuned to the same experimental data. In the figures 5 and 6 the results were compared. It can be noticed that predicted fluid phase envelopes (VLE) in both cases are quite similar, yet predictions of asphaltene phase envelope was different. In the following figures, due to the lack of experimental data measurements of lower asphaltene in publicly available literature, only upper asphaltene phase boundary was observed.

Table 1- Compositions of Fluid 2b15, injected gas and composition of mixed fluid

Components	Oil Composition [mol%]	Gas Composition [mol%]	Mixed Fluid Composition [mol%]
N2	0.32	0.59	0.3604
CO2	2.29	5.03	0.012998
H2S	0.01	0.03	2.7005
Methane	17.67	65.76	24.8795
ethane	5.25	11.32	6.1594
propane	6.14	8.58	6.5048
i-butane	1.91	2.16	1.9471
n-butane	4.72	3.62	4.5541
i-pentane	2.51	1.24	2.3191

n-pentane	3.33	1.14	3.0009
scn6	5	0.51	4.3256
scn7	5.12	0.03	4.3556
scn8	5.53	0	4.6996
scn9	4.84	0	4.1132
scn10	4.48	0	3.8072
scn11	3.78	0	3.2124
scn12	3.09	0	2.626
scn13	2.78		2.3625
scn14	2.25		1.9121
scn15	2.14		1.8186
scn16	1.79		1.5212
scn17	1.47		1.2493
scn18	1.32		1.1218
scn19	1.26		1.0708
scn20	1.15		0.9773
scn21	0.99		0.8413
scn22	0.89		0.7563
scn23	0.78		0.6629
scn24	0.7		0.5949
scn25	0.62		0.5269
scn26	0.58		0.4929
scn27	0.53		0.4504
scn28	0.49		0.4164
scn29	0.46		0.3909
c30+	3.83		3.2548

Table 2- Experimental upper AOP for Fluid 2b15

Experimental data	
Temperature [°F]	Upper AOP [psia]
255	3,125

Using PC-SAFT model it can be noticed that upper asphaltene phase boundary, that lays above bubble point, shows exponential trend. In the Figure 5 blue line represents upper asphaltene phase boundary, the blue round circle represents experimental AOP, black line below VLE curve represents lower asphaltene phase boundary, green part of VLE curve is bubble line, and purple part of VLE curve is dew line. It can be clearly seen that at constant temperature of 255 °F asphaltenes will come out of the solution at around 3,125 psia. The prediction of the model and experimental data similar, hence it can be concluded that tuning process was successful. From the graph it can be concluded that if the temperature is kept as a constant, at 255 °F, and the pressure is decreasing, asphaltenes will start coming out of solution at 3,125 psia, reach their maximal amount at bubble point (reported to be 2,100 psia, at 255 °F), and below bubble point start coming back to solution. If the problem is approached from another angle, for example if pressure of 3,125 psia is kept constant and the temperature is decreasing, asphaltenes will come out of solution again at only one point in the graph – at temperature of 255 °F. From predictions of upper asphaltene phase boundary in HydraFLASH, shown in Figure 5, it can be concluded that for one temperature only one asphaltene onset pressure can exist and vice versa.

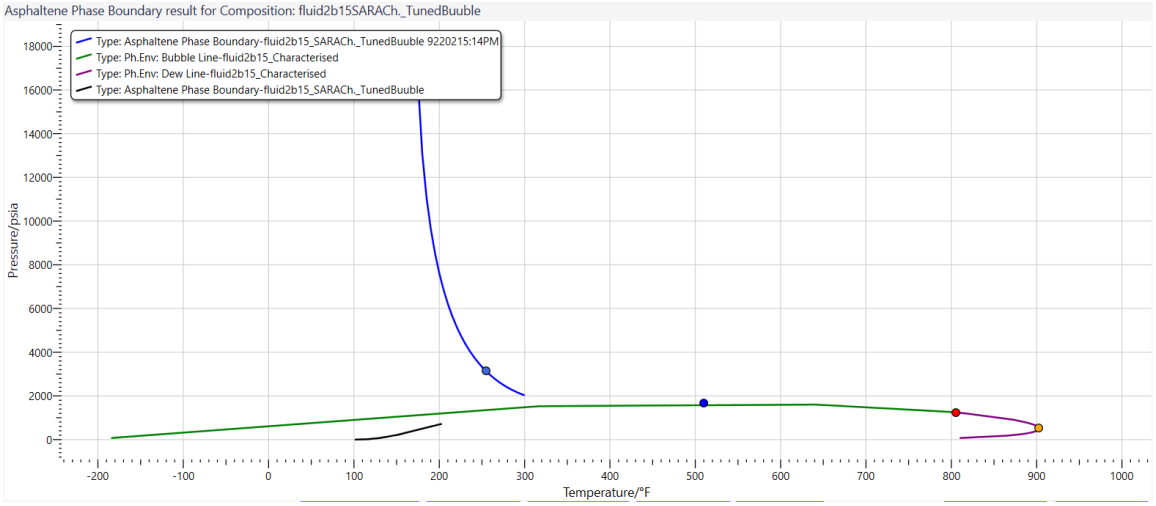


Figure 5 - Asphaltene phase behavior for Fluid 2b15 in HydraFlash, using PC-SAFT model (blue line- upper AOP, black line- lower AOP, green line – bubble line, purple line – dew line)

On the other hand, when modeling same oil composition with CPA model the results are different. In the Figure 6 blue line that lies above bubble line represents upper asphaltene phase boundary, and brown round circle that lays on it represents experimental data reported. It can be clearly seen that tuning of the model based on experimental data was successful, as model predictions and experimental data are similar. When keeping the temperature constant at 255 °F, whilst decreasing the pressure, asphaltenes will come out of solution at around 3,125 psia. On the other hand, but if pressure is kept constant at 3,125 psia and temperature was decreasing, asphaltenes will come out of solution at 255 °F as well as at temperature around 150 °F (follow arrows in the Figure 6). This observation is quite unusual for cases found in literature explaining and describing asphaltene behavior, where for one temperature only one AOP is reported.

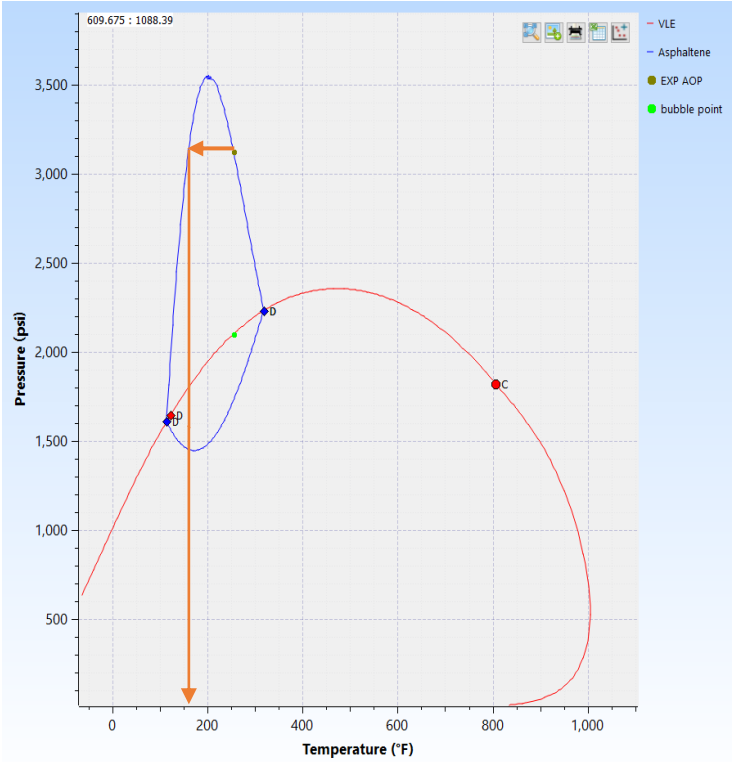


Figure 6 - Asphaltene phase behavior modeled for Fluid 2b15 in Multiflash using CPA model (blue line – upper and lower AOP boundary, red line – VLE curve)

As mentioned before, at reservoir conditions asphaltene precipitation is reversible process (Pederson et. al, 2015). At fixed temperature and pressures above bubble point asphaltenes start coming out of solution once they reach asphaltene onset pressure. At that pressure oil composition has become unfavorable for asphaltenes to be dissolve in it, and they start precipitating. What happens in general case is that once pressure is reduced to below bubble point, gas will start coming out of the solution as well, concentration of n-alkanes in oil will decrease and oil composition will become more favorable for asphaltenes. Therefore, asphaltenes will start coming back to solution with oil and completely be dissolved once again at lower asphaltene boundary (Pederson et. al, 2015). On the other hand, if the pressure is kept constant and temperature is the variable that is decreasing (as shown with arrow in the figure above), then the system will never reach bubble point and gas will not come out of solution. Hence, oil composition will not come to the stage where it will be favorable to dissolve asphaltenes and asphaltenes will not come into the solution again. It can be concluded from the graph of CPA modeling is that with decreasing the temperature at constant pressure asphaltenes will start coming out of solution when the system reaches onset pressure. They will also at some point go back to the solution, as the temperature reaches asphaltene phase boundary again. The CPA model predictions for asphaltene boundary implies that the precipitation of asphaltenes is a reversible process in terms of temperature. This observation is quite unusual for the asphaltene phase behavior described in the literature.

5.1.2. Case 2

Case 2 is an oil for which AOP was measured by depressurization (M. A. Fahim, 2007) Composition of Fluid 82 is shown in Table 3. One experimental onset pressure was reported (see

Table 4). While tuning and modeling the fluid in both software another variant behavior, related to asphaltene phase envelope was noticed.

Table 3 – Composition of Fluid 82

Component	Oil Composition [mol%]
H_2S	0
N_2	0.57
CO_2	2.46
C1	36.37
C2	3.47
C3	4.05
iC4	1.93
iC5	1.57
C6	1.62
C7	47.96

Table 4 – Experimental upper AOP for Fluid 82

Experimental data	
Temperature [K]	AOP [MPa]
373	35.6

In the following figures it can be seen that both software tuned the PC-SAFT and CPA model respectively. What happened here is that both tunings were correct but when compared different trends of asphaltene phase boundaries is seen.

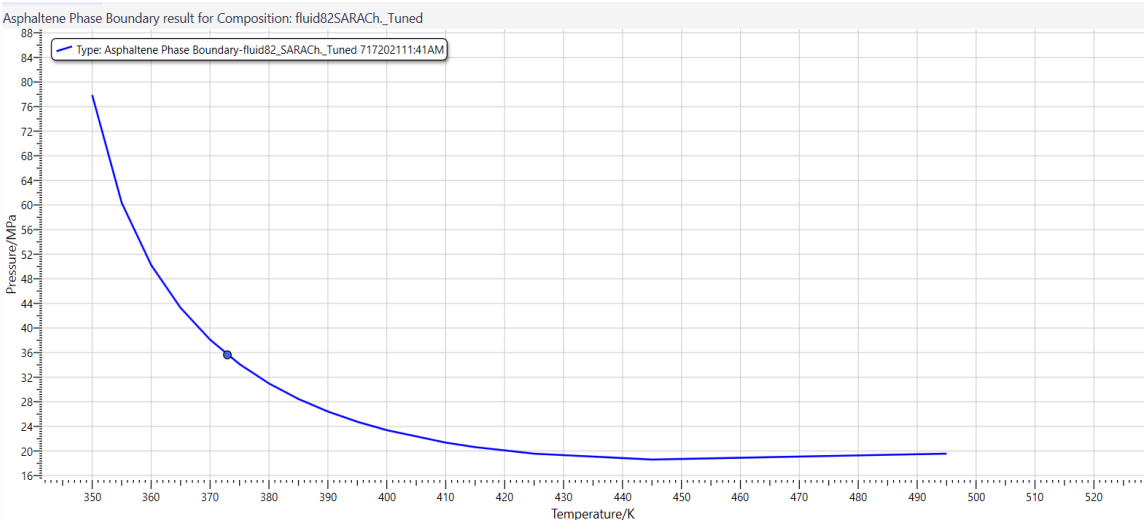


Figure 7 - Asphaltene phase behavior for Fluid 82 in HydraFLASH, using PC-SAFT model (blue line- upper AOP, blue round circle – experimental measurement of AOP)

In the figure 7 above, modeling of Fluid 82 in HydraFLASH is presented. Blue line represents upper asphaltene phase boundary, and blue round circle that lays on it represents the

experimental measurement of asphaltene onset pressure. It can be seen that tuning of model to experimental data was successful, as experimental data and predictions are similar.

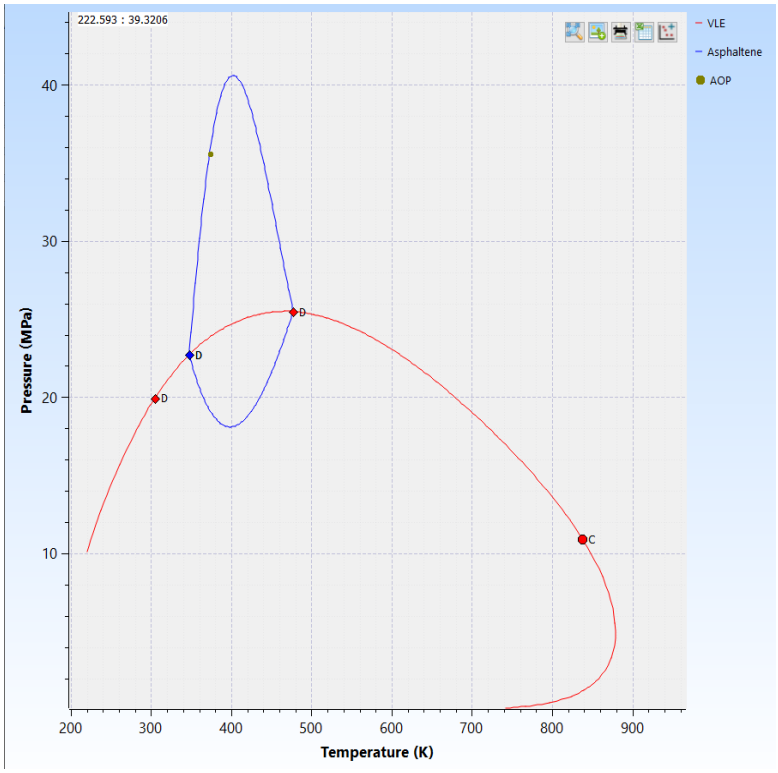


Figure 8 - Asphaltene phase behavior for Fluid 82 modeled in Multiflash using CPA model (blue line – upper and lower AOP boundary, red line – VLE curve)

The modeling and predicting of asphaltene phase behavior for the same Fluid 82 was repeated in Multiflash. In the figure above, blue line represents upper asphaltene phase boundary, and green round circle that lays on it represents experimental asphaltene onset pressure. The redline represents vapor liquid envelope. It can be seen that tuning of CPA model to experimental data was done successfully, as experimental data and predictions are similar.

In order to investigate the difference between two models predictions at another temperature (400 K), were compared. From the figure 7 according to HydraFLASH predictions of asphaltene phase behavior, asphaltene onset pressure at temperature of 400 K is around 24 MPa (see figure 9). If the same temperature is observed on asphaltene phase envelope predictions in Multiflash AOP at 400 K is around 40 MPa. This means that if predicting the phase behavior of asphaltenes one can expect asphaltenes to precipitate on much higher pressures at certain temperature when modeling with CPA model, than if modeling with PC-SAFT model.

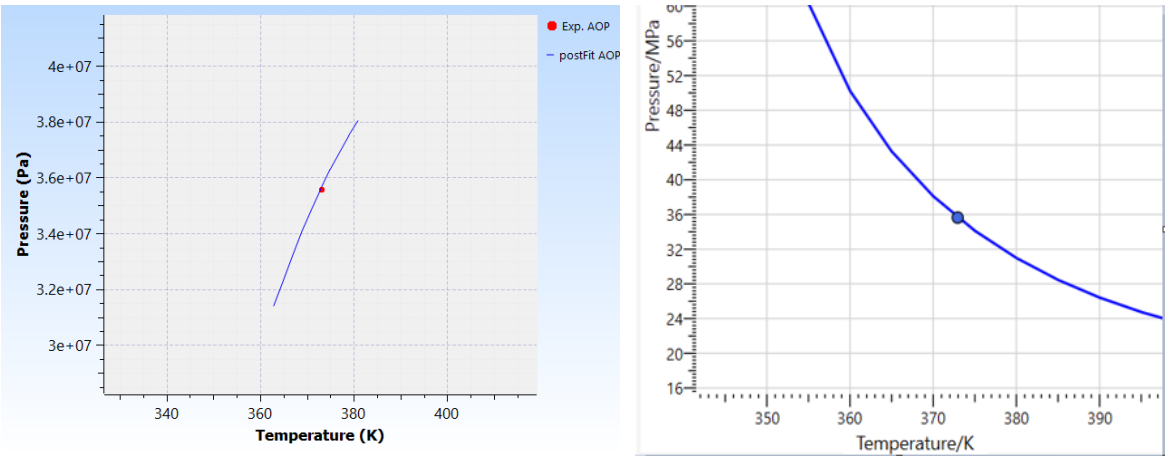


Figure 9 – Tuning the model parameters with experimental data for Fluid 82 in Multiflash (left) and HydraFLASH (right)

From Figure 9 it can be concluded that although both tunings were successful as predictions and experimental data are similar, models gave different results in predicting the upper asphaltene phase boundary (asphaltene phase boundary has different slope). PC-SAFT model (right) predictions of AOP decrease with increasing the temperature. This means that when temperature is increasing, the bonds between resin protective layer and asphaltenes will weaken and asphaltenes will come out of solution easier, at much lower pressures. With CPA model (left) if temperature is increasing then AOP is also increasing, which would mean that on higher temperatures for asphaltenes to come out of solution harder, on higher pressures. This is against normal behavior of asphaltenes.

In the previously mentioned case of Fluid 2b15, where both software tuned the thermodynamic model with experimental data with the same slope of asphaltene envelope, predictions of asphaltenes onset pressure boundary were similar. On the other hand, when both models tuned experimental data with different slope of asphaltene phase boundary, the results are very different.

5.1.3. Case 3

As mentioned before, CPA model gave most of the predictions phase envelope with parabolic shape. In some cases, such as Case 3, CPA model gave same predictions, in terms of shape, as PC-SAFT. In the following example, oil composition (see table 5) was modeled in both software and results were compare. The AOP was measured with depressurization and only one experimental AOP was reported (M. A. Fahim, 2007). Experimental AOP data is presented in table 6. In can be seen that both models were tuned the experimental data successfully, and both models predicted similar asphaltene phase behavior.

Table 5 – Composition of Fluid 83

component	Oil composition [mol%]
H_2S	0
N_2	0.97
CO_2	0.2
C1	27.55
C2	7.43

C3	9.02
iC4	6.14
iC5	4.16
C6	3.16
C7	41.39

Table 6 – Experimental measurments of AOP for Fluid 83

Experimental data	
Temperature [K]	AOP [MPa]
365	20.1

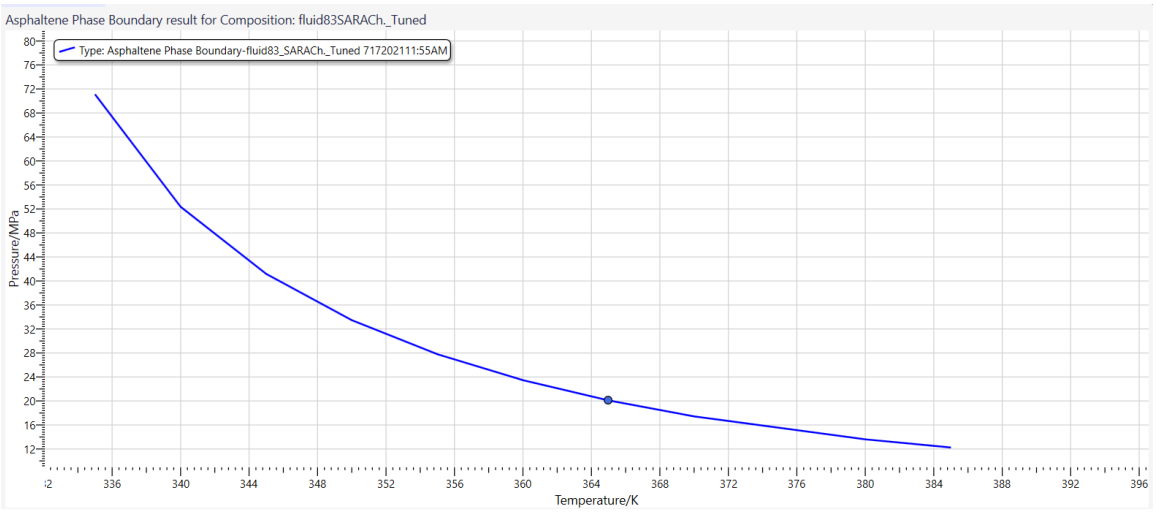


Figure 10 - Asphaltene phase behavior for Fluid 83 in HydraFLASH, using PC-SAFT model (blue line- upper AOP, blue round circle – experimental measurement of AOP)

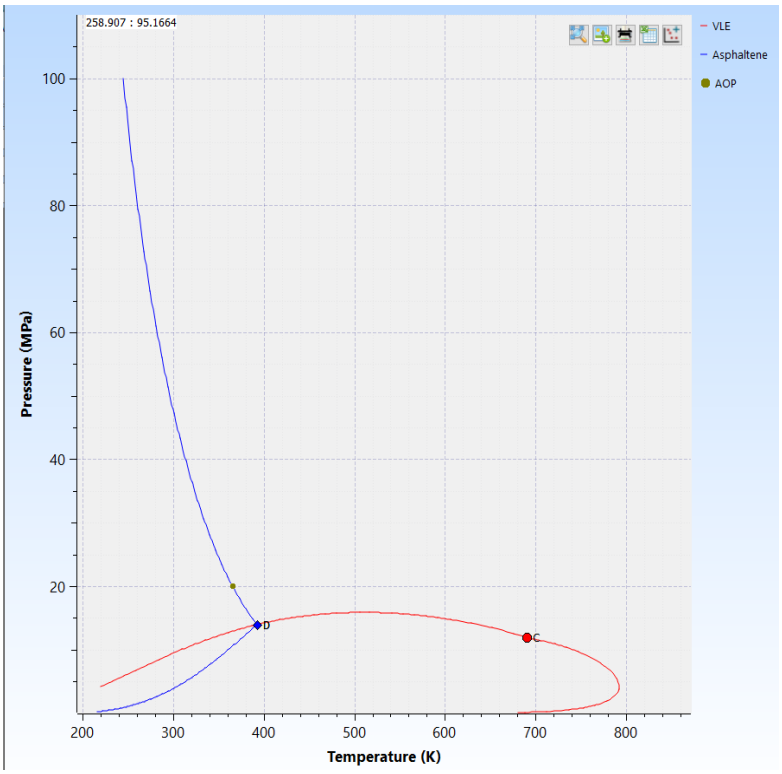


Figure 11 - Asphaltene phase behavior for Fluid 83 modeled in Multiflash using CPA model (blue line – upper and lower AOP boundary, red line – VLE curve)

5.2. How Multiflash Adjusts the Asphaltene Model Using Experimental Data

In the process of gathering the data for experimental study, it was noticed that one data set reported in the literature is not describing the asphaltene behavior as expected (with decrease of temperature AOP should increase). The composition of oil modeled in this case is presented in table 7. The AOP was measured with depressurization and 3 experimental AOPs were reported (Sullivan et. al. 2020)

Table 7 – Composition of Fluid 3b

Component	Oil composition [mol%]
CO_2	1.304
H_2S	0
N_2	0.316
C_1	34.471
C_2	8.97
C3	7.215
i-C4	1.182
n-C4	3.389
i-C5	1.531
n-C5	1.99
C6	2.929

methylcyclopentane	0.346
Benzene	0.135
cyclohexane	0.224
C7	2.399
methylcyclohexane	0.465
Toluene	0.383
C8	2.47
ethylbenzene	0.174
m-xylene	0.33
o-Xylene	0.244
C9	2.299
C10	2.558
C11	2.163
C12	1.791
C13	1.856
C14	1.518
C15	1.393
C16	1.171
C17	1.064
C18	0.982
C19	0.97
C20	0.804
C21	0.74
C22	0.67
C23	0.612
C24	0.561
C25	0.509
C26	0.475
C27	0.448
C28	0.415
C29	0.404
C30+	6.13

In the table 8 below experimental data of asphaltene onset pressure of the data set in the matter is presented.

Table 8 – Experimental AOP for Fluid 3b

Experimental data for AOP	
T [°C]	AOP [psia]
75	5000
100	5500
125	5000

As seen values reported in the table 8 for upper AOP are not describing normal behavior of asphaltenes. As mentioned before, with decreasing temperature upper asphaltene onset pressure increases. If the behavior of asphaltenes was normal, at temperature of 75 °C, AOP would be higher than at temperature of 100 °C. Regardless the error, the data was modeled in both software to compare whether the software will recognize the error at lowest temperature and predict asphaltene behavior based on experimental data that was reported for other two temperatures. In the following figures modelling results are presented.

In the figure below prediction of upper asphaltene phase boundary for Fluid 3b in HydraFLASH is presented. It can be seen that the PC-SAFT model predictions after tuning perfectly matched only one experimental point. However, predicted upper AOPs for lowest and the highest temperature reported did not match good with experimental data. It can be noticed that HydraFLASH did give good trend of asphaltene phase boundary, and that one can get understanding from this graph how would asphaltenes behave, although it the tuning was not perfect.

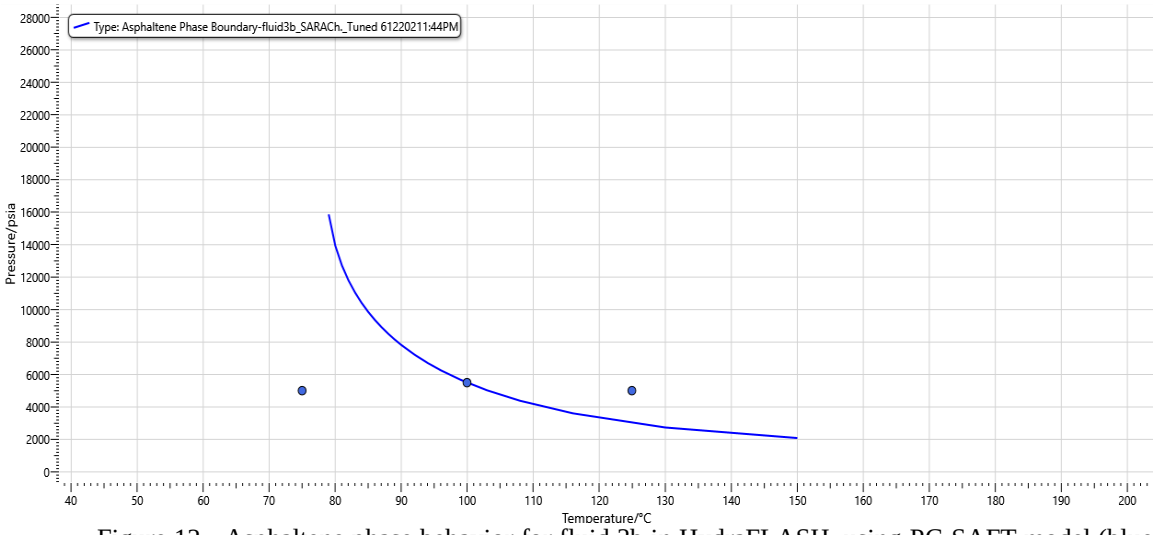


Figure 12 - Asphaltene phase behavior for fluid 3b in HydraFLASH, using PC-SAFT model (blue line- upper AOP, blue round circles – experimental measurement of AOP)

The tuning procedure was repeated in Multiflash, as well. In the figure 13 tuning the CPA model to the experimental data for fluid 3b in Multiflash is presented. It can be noticed that tuning of model to experimental data was mathematically better than that performed using the PC-SAFT model. In the figure 14 prediction of asphaltene phase behavior is shown. The unusual shape of asphaltene phase boundary is once again seen in the CPA model predictions. It can be concluded that both software gave different results. Tuning procedure in both software was repeated for only two experimental points (at 100 °C and 125 °C) and the similar results were obtained. HydraFLASH did not match perfectly, but the shape of asphaltene phase behavior met the expectations. However, Multiflash tuned perfectly with experimental data, but the predictions were like in the case explained earlier, when model parameters were tuned with all three experimental measurements from table 8.

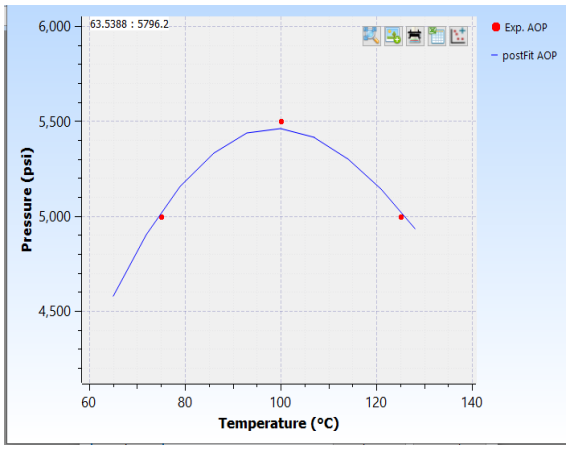


Figure 13 – Tuning the CPA model to experimental AOP for fluid 3b (blue line – asphaltene phase oundary, red rounded circles – experimental AOP)

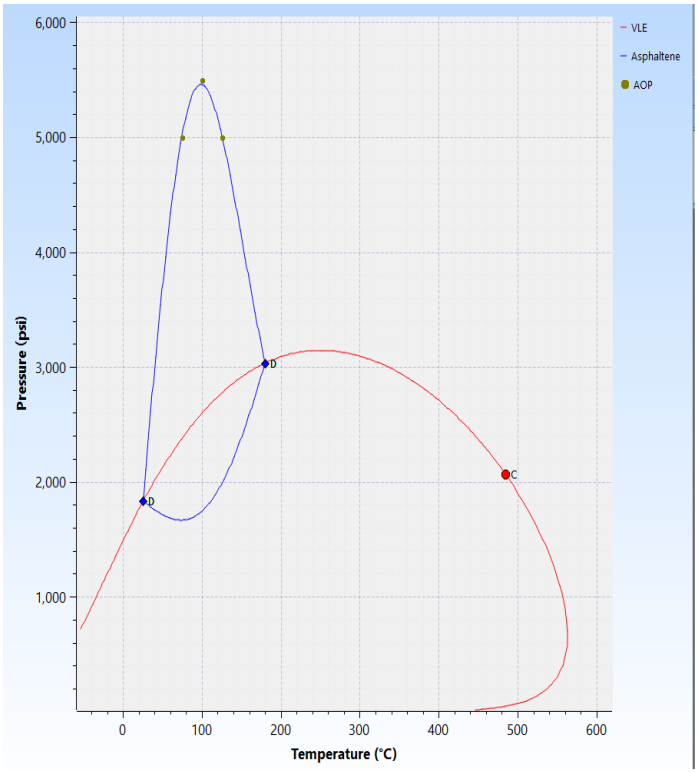


Figure 14 - Asphaltene phase behavior for fluid 3b modeled in Multiflash using CPA model (blue line – upper and lower AOP boundary, red line – VLE curve)

This situation raised a question of reliability of modeling with CPA model in Multiflash software. To test if Multiflash software will match wrong data, just for the sake of obtaining mathematically perfect matching, one experimental data set was altered on purpose. Composition of fluid 4a (Jamaluddin et. al. 2002) is presented in table 9. Both, CPA and PC-SAFT models were tuned to this experimental data in software and results were compared. The composition of oil that was modeled for this purpose is presented in table below.

Table 9 – Composition of Fluid 4a

Components	Oil Composition
Nitrogen	0.49
Carbon Dioxide	11.37
Hydrogen Sulfide	3.22
Methane	27.36
Ethane	9.41
Propane	6.7
I - Butane	0.81
N - Butane	3.17
I - Pentane	1.22
N - Pentane	1.98
SCN6	2.49
scn7	2.87
scn8	3.14
scn9	2.74
scn10	2.32
scn11	1.9
C12+	18.82

In the table below experimental data set before and after the change of one asphaltene onset pressure is presented:

Table 10 - Experimental AOP for Fluid 4a before and after the change

Original experimental data		Experimental data after the change of AOP	
Temperature [°F]	AOP [psia]	Temperature [°F]	AOP [psia]
190	5400	190	3500
230	4050	230	4050
260	3650	260	3650
300	3800	300	3800

In the table above the asphaltene onset pressure at the temperature of 190°F was decreased on purpose, to be much lower that the value on temperature of 230 °F (highlighted row). In the figures below, first the modeling before the change is presented, and then the results after the change are presented and results are compared.

The figure 15 shows tuning of PC-SAFT model in HydraFLASH software to the original experimental data. It can be noticed that tuning of the model to the experimental data was successful as experimental data is similar to predictions of asphaltene behavior.

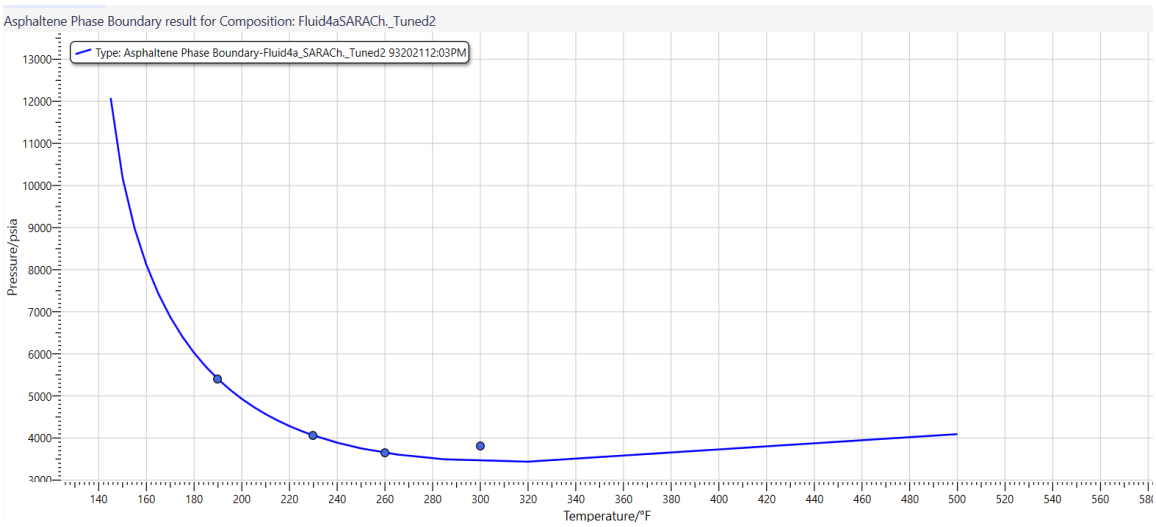


Figure 15 - Asphaltene phase behavior for fluid 4a (before the change of experimental data) in HydraFLASH, using PC-SAFT model (blue line- upper AOP, blue round circles – experimental measurement of AOP)

In the figure below the tuning of the model to the altered data set of asphaltene onset pressures is shown. It can be noticed that PC-SAFT model did not try to tune the EOS with experimental data that was changed on purpose, and it gave logical trend and behavior of asphaltene phase, regardless the wrong data input.

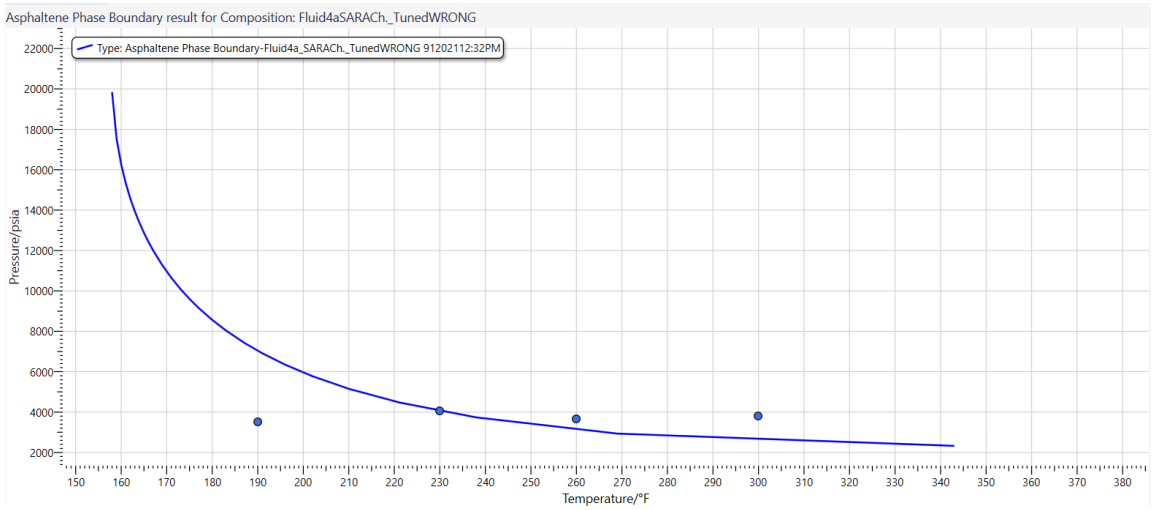


Figure 16 - Asphaltene phase behavior for fluid 4a (after the change of experimental data) in HydraFLASH, using PC-SAFT model (blue line- upper AOP, blue round circles – experimental measurement of AOP)

On the other hand, the tuning of the CPA model to the original experimental data in Multiflash, shown in the figure below, was not as successful as tuning in HydraFLASH. The model did not manage to tune to last two experimental measurements. However, the purpose of this experiment was to show whether the CPA model will change after the experimental data was altered.

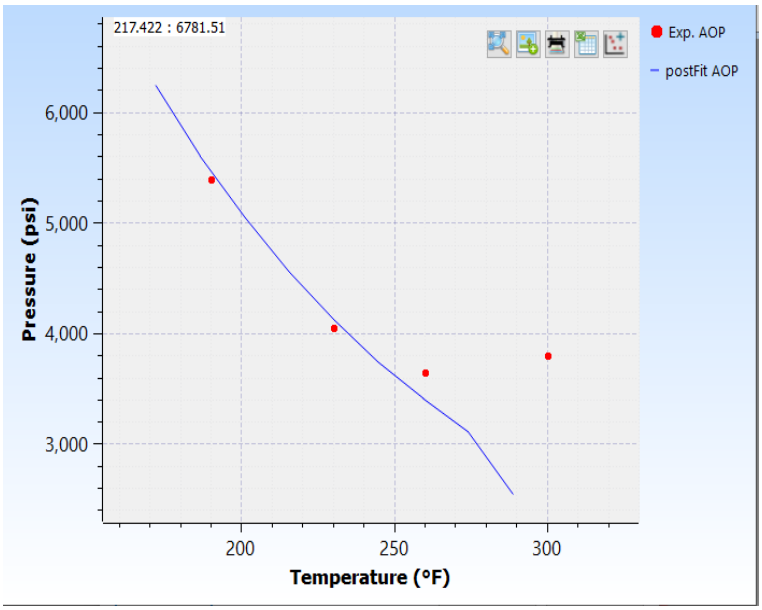


Figure 17 - Tuning the CPA model to original experimental AOP for fluid 4a (blue line – asphaltene phase oundary, red rounded circles – experimental AOP)

In the figure below, that modeling with CPA model turned out completely different. The Multiflash tried to accomplish perfect mathematical modeling with experimental data and gave completely wrong results.

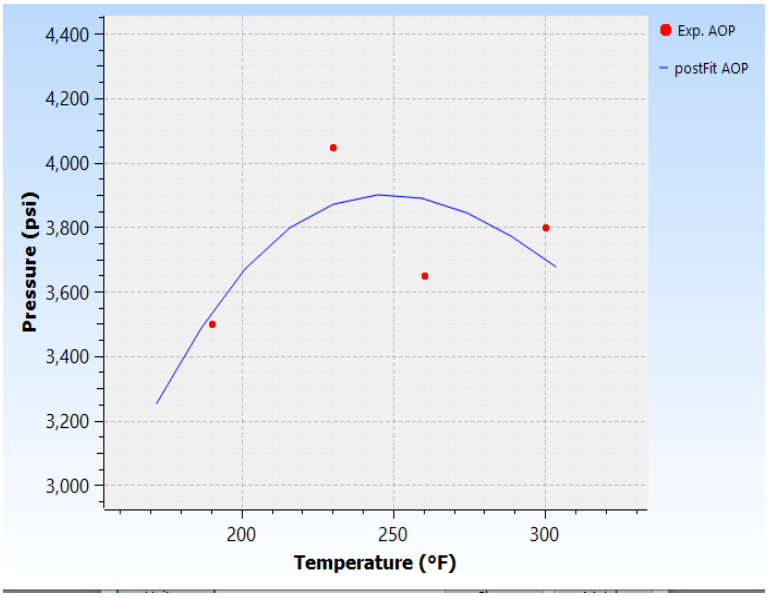


Figure 18 - Tuning the CPA model to altered experimental AOP for fluid 4a (blue line – asphaltene phase oundary, red rounded circles – experimental AOP)

In the following figures the prediction in Multiflash were compared when the CPA model was tuned with original data (figure 19) and with altered data (figure 20). It can be noticed that the prediction changed completely, while PC- SAFT model recognized the error in experimental data, excluded it and tuned the model parameters to other three correct experimental points.

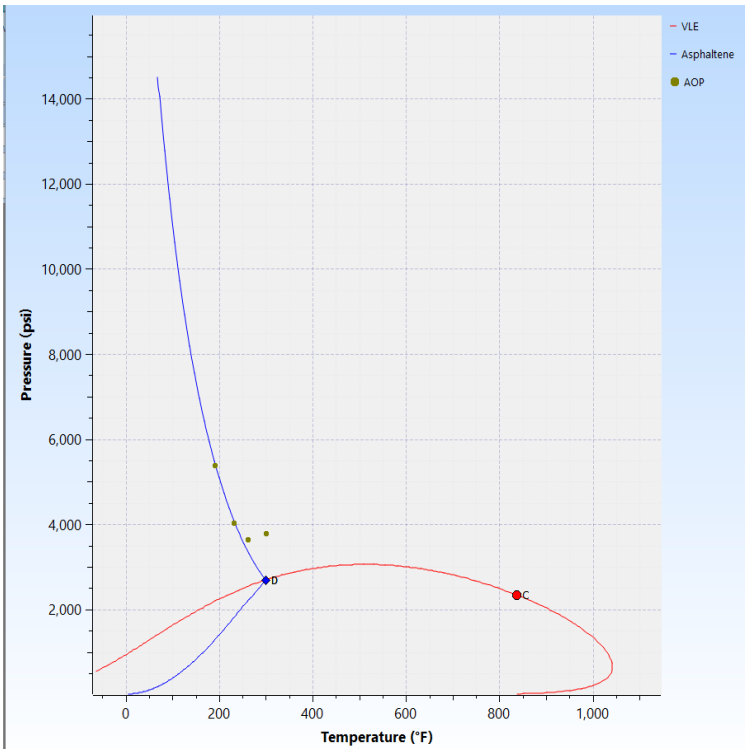


Figure 19 - Asphaltene phase behavior for fluid 4a (before the change of experimental data) modeled in Multiflash using CPA model (blue line – upper and lower AOP boundary, red line – VLE curve)

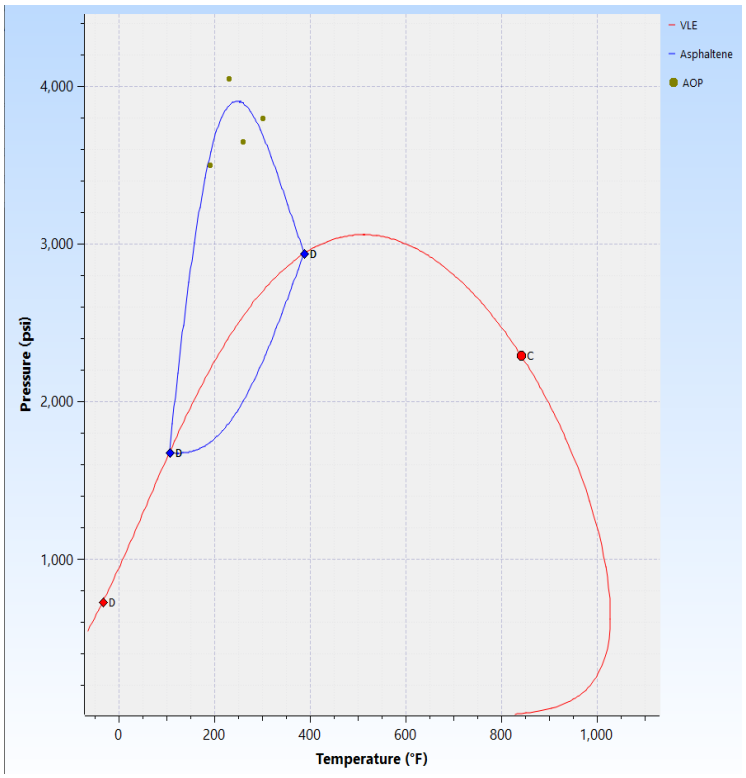


Figure 20 - Asphaltene phase behavior for fluid 4a (after the change of experimental data) modeled in Multiflash using CPA model (blue line – upper and lower AOP boundary, red line – VLE curve)

5.3. Tuning the models

When creating the asphaltene model in software there are few steps that are common for both HydraFLASH and Multiflash. The first step is creating the fluid, where both software require composition of a live fluid. Second step is characterizing the fluid using SARA analysis data. When fluid is characterized asphaltene model parameters must be tuned based on experimental data. This step is called tunning, and it requires data which including AOP data (both lower and upper onset pressure would be ideal), saturation properties, such as bubble point and saturation density. Models can be tuned differently based on technique used for measuring the asphaltene onset pressure: if the asphaltene onset pressure was measured by depressurization then model can be tuned to asphaltene data with AOP data or with both AOP and saturation data; and if the asphaltene onset pressure was measured by using titration method then model can be tuned with experimental data also by titration test data, such as n-heptane and n-pentane amount used for unit volume of dead oil in the experiment.

Data used in this thesis had two types of experimental data: AOP measurements with depressurization and AOP measurements with gas injection. In both cases models were tuned to experimental data with only AOP and with AOP and saturation properties and results were compared.

In the following the difference between model tuning with AOP data and with both AOP and saturation data are presented.

5.2.1 Case 1

The purpose of presenting Case 1 is to show difference between asphaltene phase boundaries when asphaltene model is tuned with AOP data and when asphaltene model is tuned with both AOP and saturation data. The composition of oil that was modeled in case 1 is presented was presented in chapter 5.1.4. in table 9 and experimental AOP is presented in table 11. Both cases are compared in each of the software and the results are presented below (see figures 21-25).

Table 11 – Experimental measurment of AOP and Bubble Pressure for Fluid 4a

temperature [°F]	Precipitation Pressure [psia]	Bubble Pressure [psia]
190	5400	2500
230	4050	2700
260	3650	2900
300	3800	3060

In the figure below tuning model parameters with experimental data was done only based on AOP experimental data. This fluid composition had 4 experimental measurements reported. All 4 experimental asphaltene onset pressures were used in tuning model parameters and predicting upper asphaltene phase boundary. As illustrated in the figure 21 the tuning procedure was successful. Absolute average error reported by software was 1.79 %.

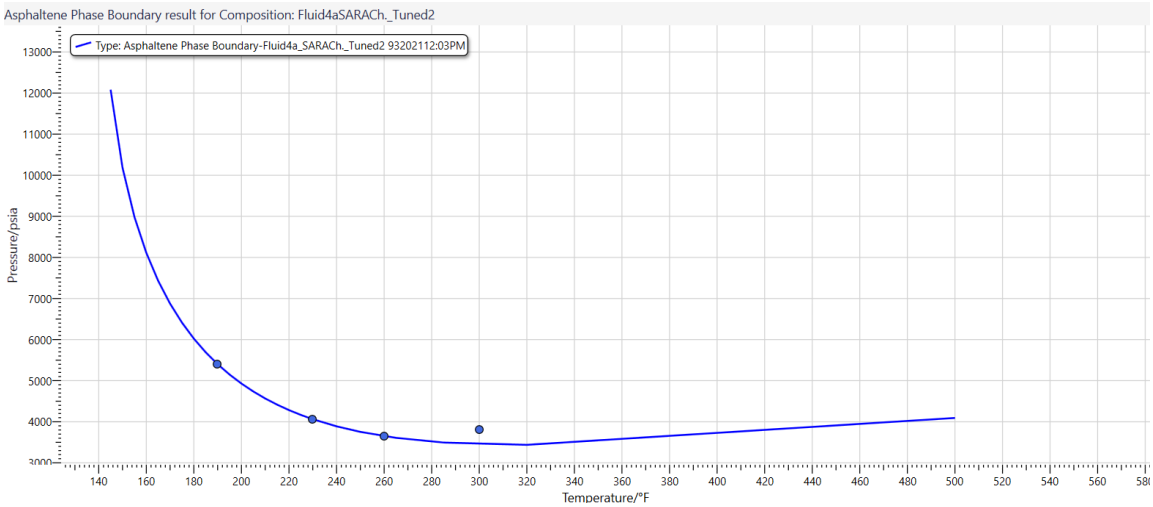


Figure 21 - Asphaltene phase behavior for fluid 4a after tunning the model with experimental AOP in HydraFLASH, using PC-SAFT model (blue line- upper AOP, blue round circles – experimental measurement of AOP)

In the figure below tuning of model parameters to experimental data of previously mentioned oil was done with AOP and saturation pressure (bubble point) data. Bubble point data was measured at 4 different temperatures, and this experimental data, as well as AOP at 4 different temperatures were used for tuning the model parameters (reported in Table 11). It can be noticed that tuning was not as successfully done as in the previous case, where model parameters were tuned with only AOP experimental data. Absolute averaged error reported was 21.17 %.

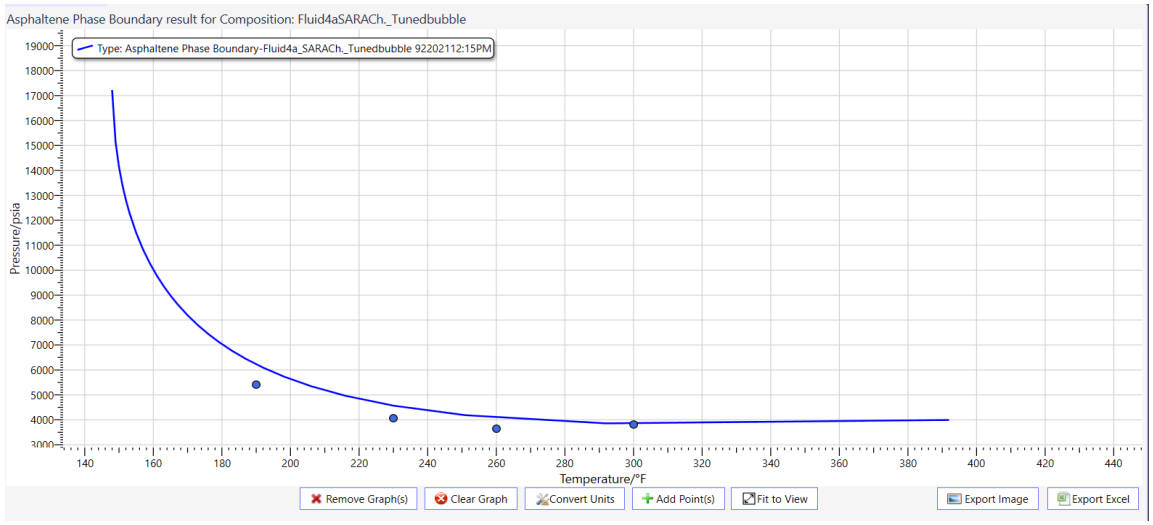


Figure 22 - Asphaltene phase behavior for fluid 4a after tunning the model with experimental AOP and saturation data in HydraFLASH, using PC-SAFT model (blue line- upper AOP, blue round circles – experimental measurement of AOP)

For better comparison of both tuning results and better clarification of the results of Case 1, both models were compared in one graph and reported in the figure below. Green line in the figure represents model tuned with both AOP and saturation data, while blue line represents model tuned with only AOP data. It can be concluded that tuning the model parameters with both AOP and saturation data caused bigger absolute error and asphaltene phase envelope shifted towards higher pressures. If one temperature was observed, for example 180 °F it can be clearly

seen that if model is tuned with only AOP then asphaltenes can be expected to come out of solution at around 6,000 psia. If model is tuned with both AOP and saturation pressure asphaltenes can be expected to come out of solution at much higher pressure of around 7,000 psia. It can be noticed that pressure difference between both models increases with temperature decrease. Bubble pressure on reservoir temperature of 296 °F for this oil composition was reported to be 3,045 psia. When this pressure and temperature are observed in the figure below it can be concluded that difference between two models is lowest at this point, and it increases with decrease of pressure and temperature.

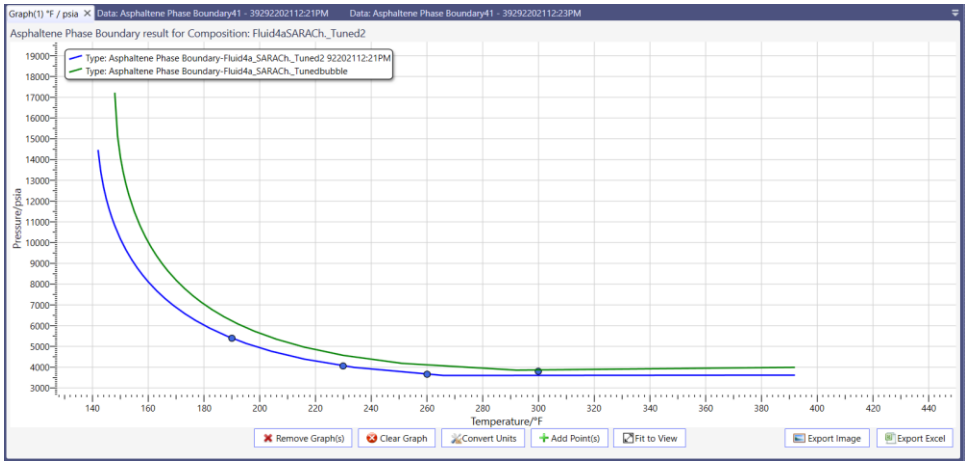
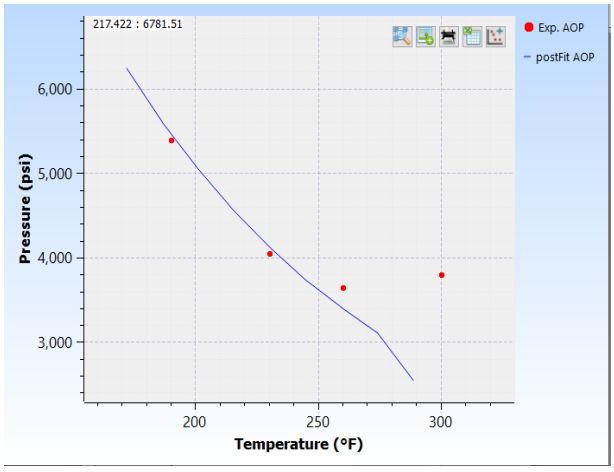
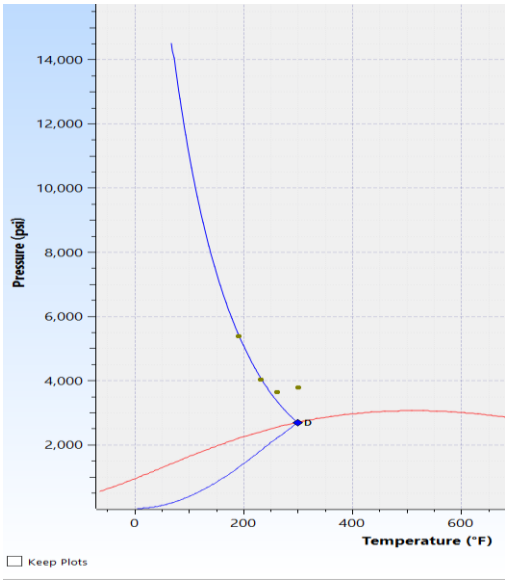


Figure 23 – Comparison of predictions of asphaltene phase bahavior when model is tuned with AOP data (blue line) and when model is tuned with AOP and saturation data (green line) for the Fluid 4a

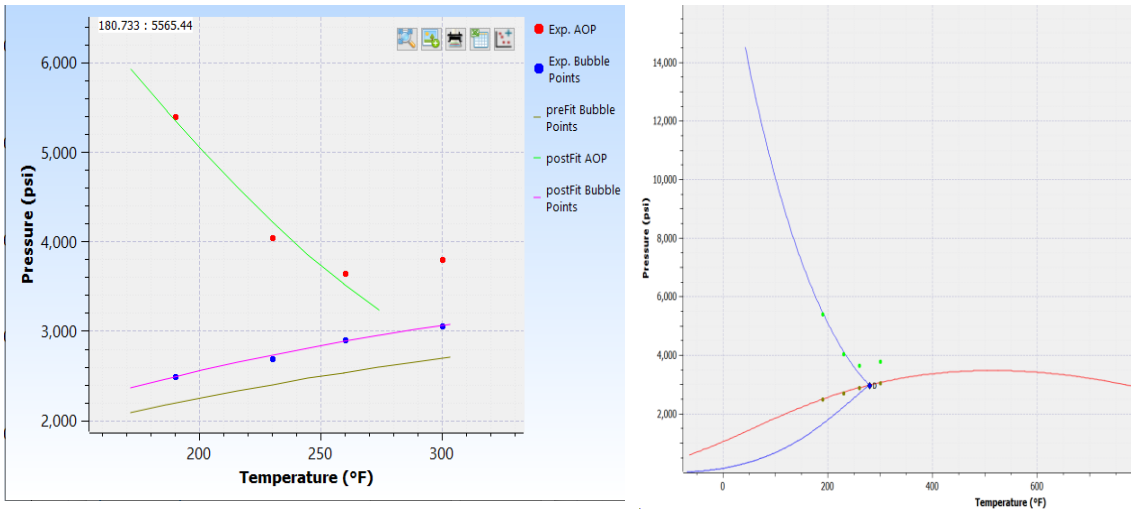
Same procedure was repeated in Multiflash. Tuning was less successful than in HidraFLASH. It can be noticed that model parameters were successfully tuned to only two out of four experimental points. The tuning (left) and asphaltene phase boundary (right) when model parameters are tuned with only AOP experimental data are presented below.



(a)



(b)



(c) (d)

Figure 24 – Tuning the model with experimental data for Fluid 4a in Multiflash using CPA model (a) Tunning the model parameters with experimental AOP data, (b) predictions of asphaltene behavior when model is tuned with AOP data, (c) tuning the model with experimental AOP and saturation data, (d) predictions of asphaltene phase behavior when model is tuned with AOP and saturation data, red line – VLE curve)

For better comparison of both tuning results and better clarification of the results of case 1 both models were compared in one graph and reported in the figure 25. Green line in the figure represents model tuned with both AOP and saturation data, while blue line represents model tuned with only AOP data. It can be concluded that tuning the model parameters with both AOP and saturation data and tuning the model with only AOP data did not make big difference in the results of tuning in Multiflash. After comparing both tuning cases it can be noticed that CPA model parameter were tuned to experimental data almost the same both times, unlike the PC-SAFT model. Bubble pressure on reservoir temperature of 296 °F for this oil composition was reported to be 3,045 psia. When this pressure and temperature are seen in the figure below it can be concluded that difference between two models is lowest at this point, and it increases with decrease of pressure and temperature. The biggest difference between both predictions is at higher pressures. Difference between both predictions can be observed in VLE as well, where VLE of fluid that was tuned with both AOPs and saturation data shifted upwards. This means that calculation of phase envelope without tuning the fluid to saturation data was not as successful as after the tuning the model with saturation data. This difference cannot be noticed in Hydraflash, because of difference in operating of two software. The reason is that, in order to calculate VLE curve in Hydraflash, fluid is separately characterized, and VLE calculation is not connected to calculation of asphaltene, while in Multiflash there are no separate characterization for VLE curve and asphaltene phase boundary. They are both automatically calculated with only one characterization.

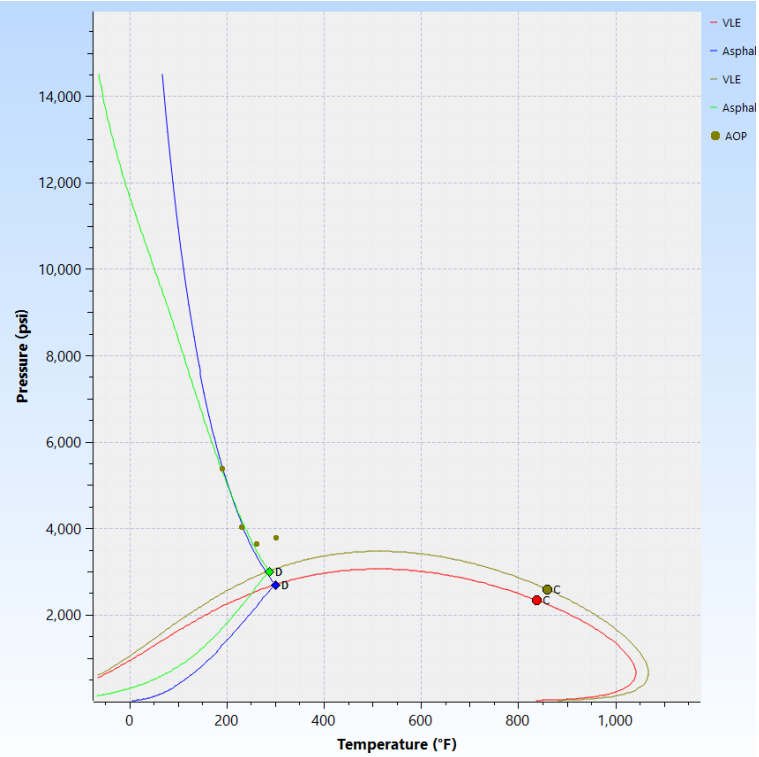


Figure 25 – Comparison of asphaltene phase behavior for Fluid 4a modeled in Multiflash using CPA model (blue line – prediction of upper and lower AOP boundary after tunning the model with AOP and saturation data, red line – VLE curve after tunning the model with AOP and saturation data, green line- prediction of asphaltene phase behavior after tunning the model with AOP data, brown line- VLE curve after tunning the model with AOP data)

5.2.2. Case 2

The purpose of the Case 2 is to present the error in tuning noticed in HydraFLASH software. The composition of oil modeled in Case 2 is presented in Table 12 and experimental AOP and bubble pressure are presented in Table 13 (M. A. Fahim, 2007).

Table 12 – Composition of the Fluid 85

Components	Oil Composition
H2 S	0.37
N2	0.09
CO2	1.22
C1	23.99
C2	10.14
C3	8.39
iC4	5.33
iC5	4.39
C6	4.69
C7	42.19

Table 13 – Experimental measurments of AOP and bubble pressure for Fluid 85

Experimental data		
Temperature [K]	AOP [MPa]	Bubble Pressure [MPa]
386	27.4	12.6

In the figure 26 both tuning with AOP data and tuning with AOP and saturation data is presented. Green line represents asphaltene phase boundary when model is tuned with only AOP data. It can be noticed that tuning was successful. Blue line on the other hand represents asphaltene phase boundary when model is tuned with both saturation properties and AOP data.

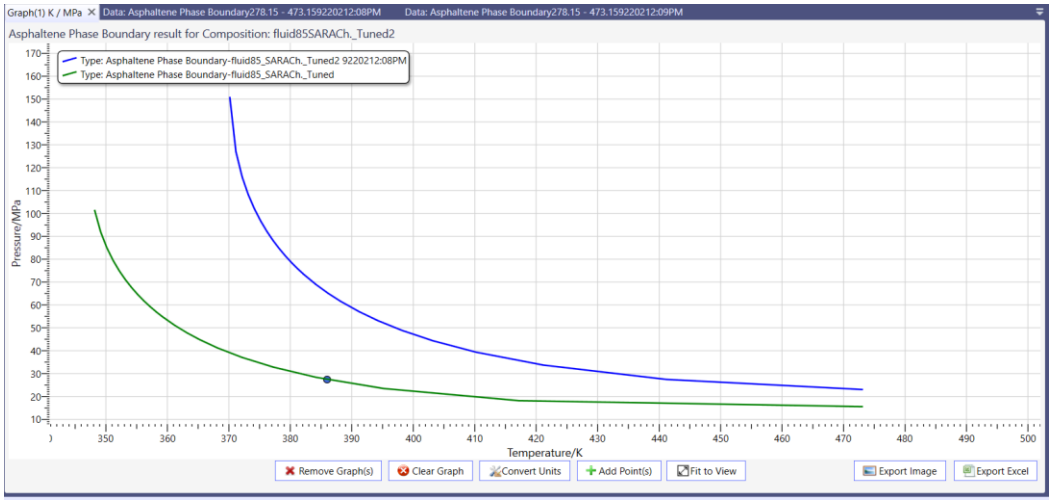


Figure 26 - Comparison of predictions of asphaltene phase bahavior in HydraFLASH when model is tuned with AOP data (blue line) and when model is tuned with AOP and saturation data (green line) for the fluid 85

In order to confirm if saturation properties were reported correctly, the same procedure was done in MultiFlash. In the figure bellow blue line represents asphaltene phase boundary when model is tuned with only AOP data and green line represents asphaltene phase boundary when model is tuned with both AOP and saturation data. It can be seen that both tuning cases gave good results. Two asphaltene phase boundaries differ only at higher pressures and lower temperatures but tuning the model parameters to experimental data was done successful.

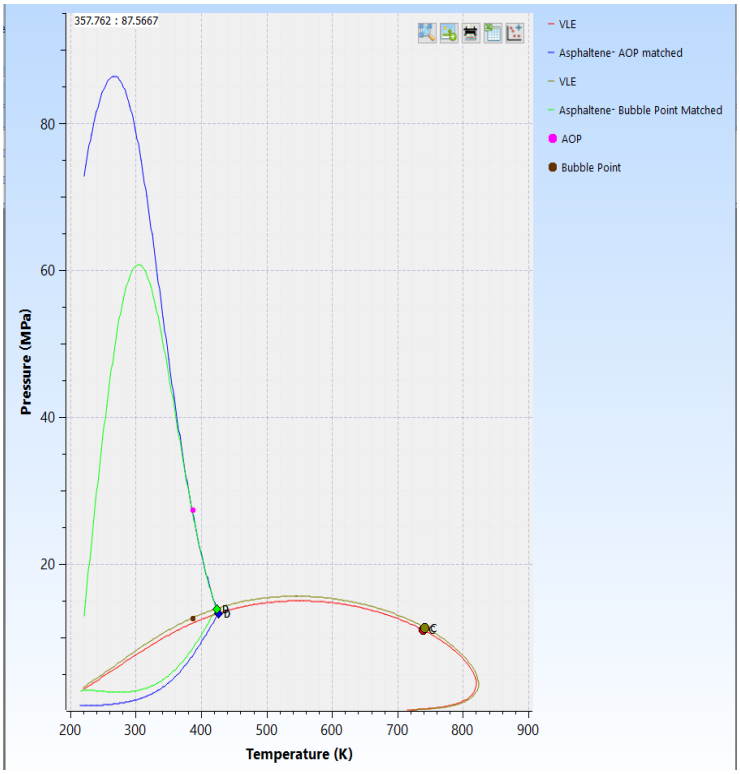


Figure 27 - Comparison of asphaltene phase behavior for Fluid 85 modeled in Multiflash using CPA model (green line – prediction of upper and lower AOP boundary when tunning the model with AOP and saturation data, red line – VLE curve after tunning the model with AOP and saturation data, blue line- prediction of asphaltene phase behavior when tunning the model with AOP data, brown line- VLE curve after tunning the model with AOP data)

In the figure below, tuning with AOP and saturation properties for Fluid 85 in Hydraflah is presented, together with VLE curve. When results are compared with results from Multiflash software, it can be concluded that tuning with AOP and saturation properties was done much better by CPA model. As far as the VLE, it was calculated good by both software.

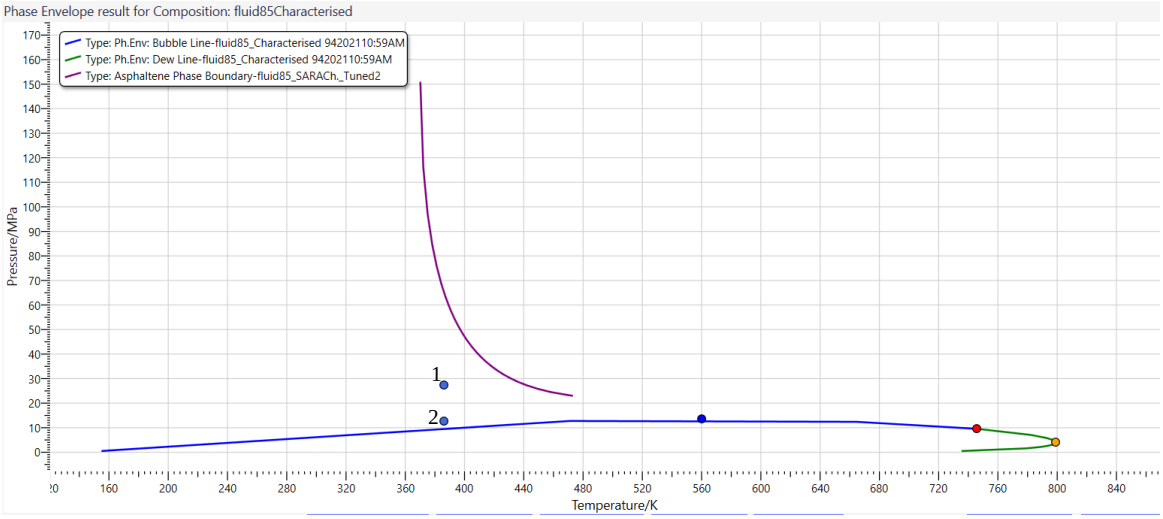


Figure 28 Predictions of asphaltene phase bahavior in HydraFLASH when model is tuned with AOP and saturation data (purple line) for the fluid 85 (blue round circle 1- experimental AOP, blue round circle 2 – experimental bubble pressure, blue line – bubble line, greeen line – dew line)

In the figures below case where HydraFLASH did a good in tuning with only AOP and did not converge the calculation of tuning with AOP and saturation pressures is presented. Multiflash gave good tuning and prediction of asphaltene phase behavior.

Table 14 – Composition of Fluid 6a

components	Oil composition [mol%]
Nitrogen	0.48
Carbon Dioxide	0.92
Hydrogen Sulfide	0
Methane	43.43
Ethane	11.02
Propane	6.55
i Butane	0.79
n Butane	3.7
i Pentane	1.28
n Pentane	2.25
n hexane	2.7
C7+	26.88

Table 15 – experimental AOP and bubble point for Fluid 6a

Temperature [°C]	Upper AOP [MPa]	Bubble Pressure [Mpa]
99	47.26	22.21
104	45.42	22.64
110	44.26	22.59
116	42.92	22.68

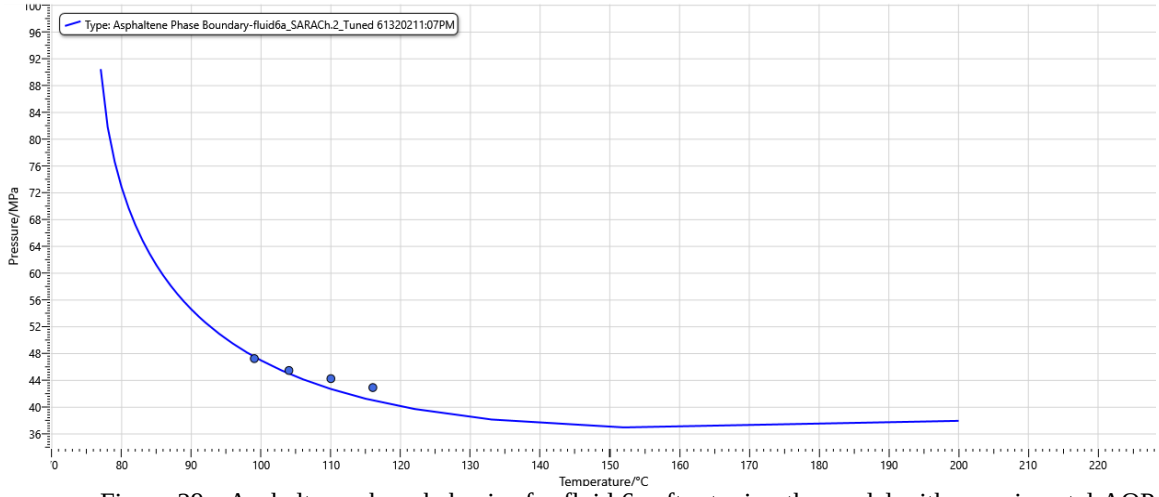


Figure 29 - Asphaltene phase behavior for fluid 6a after tuning the model with experimental AOP data in HydraFLASH, using PC-SAFT model (blue line- upper AOP, blue round circles – experimental measurement of AOP)

As seen in figure 29 tuning the model parameters to experimental AOP was successful as experimental data is similar to predictions. Tuning the model parameters to experimental data of both AOP and saturation properties is shown in figure 30. The tuning was not successful and

calculations of asphaltene phase boundary did not converge because of software bug. On the other hand, tuning and predicting asphaltene phase behavior in Multiflash, resented in figures 31 and 32 was successful.

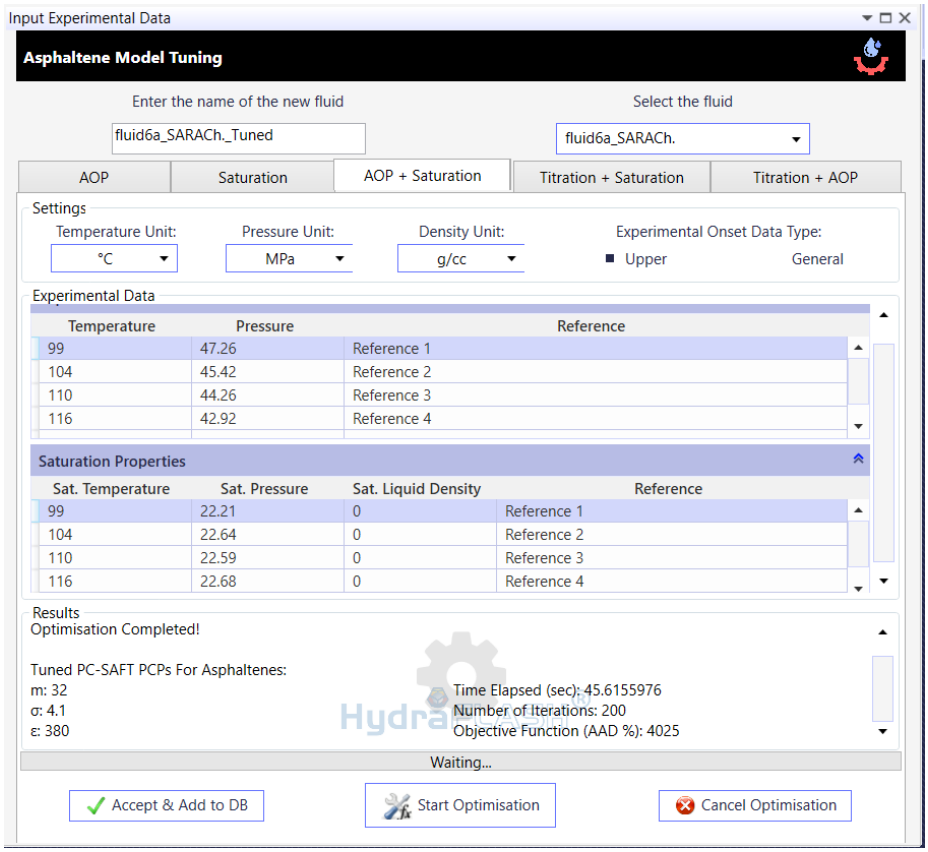


Figure 30 – Tuning of model parameters to experimental data in HydraFASH for fluid 6a

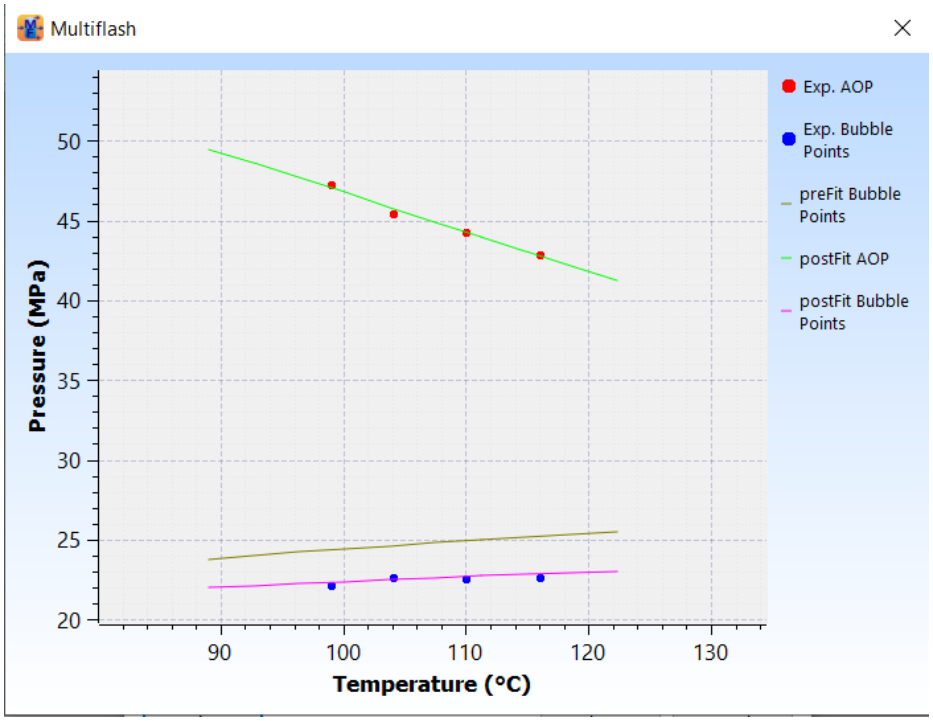


Figure 31 – Tuning the model parameters to experimental data in Multiflash for fluid 6a

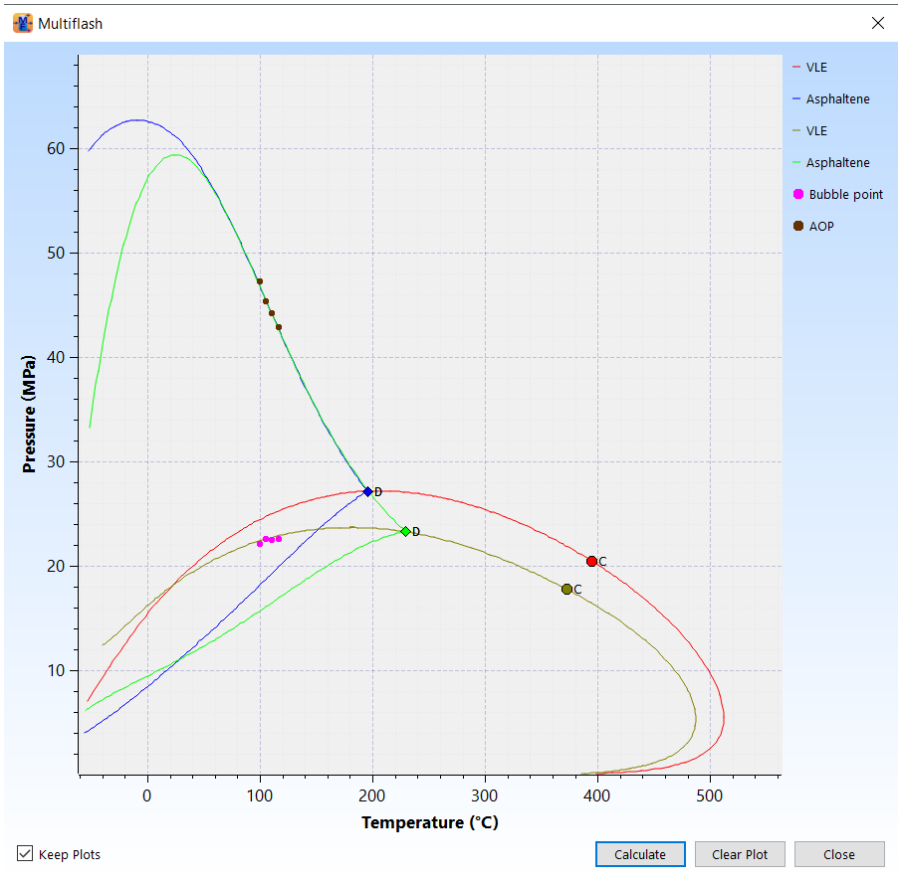


Figure 32 - Comparison of asphaltene phase behavior for fluid 6a modeled in Multiflash using CPA model (green line – prediction of upper and lower AOP boundary when tunning the model with AOP

and saturation data, brown line – VLE curve after tunning the model with AOP and saturation data, blue line- prediction of asphaltene phase behavior when tunning the model with AOP data, red line- VLE curve after tunning the model with AOP data)

In the Figure 32 it can be seen how Multiflash adjusts the VLE curve based on tuning the model with saturation properties (there are two VLE curves – one when model is tuned with only AOP and one when model is tuned with AOP and saturation properties).

The problem that occurred in Hydraflash software during modeling was that in matching the data with AOP and saturation properties did not converge because of high absolute error in several cases. The results of models that gave big absolute error are presented in the figures below and compared to Multiflash results.

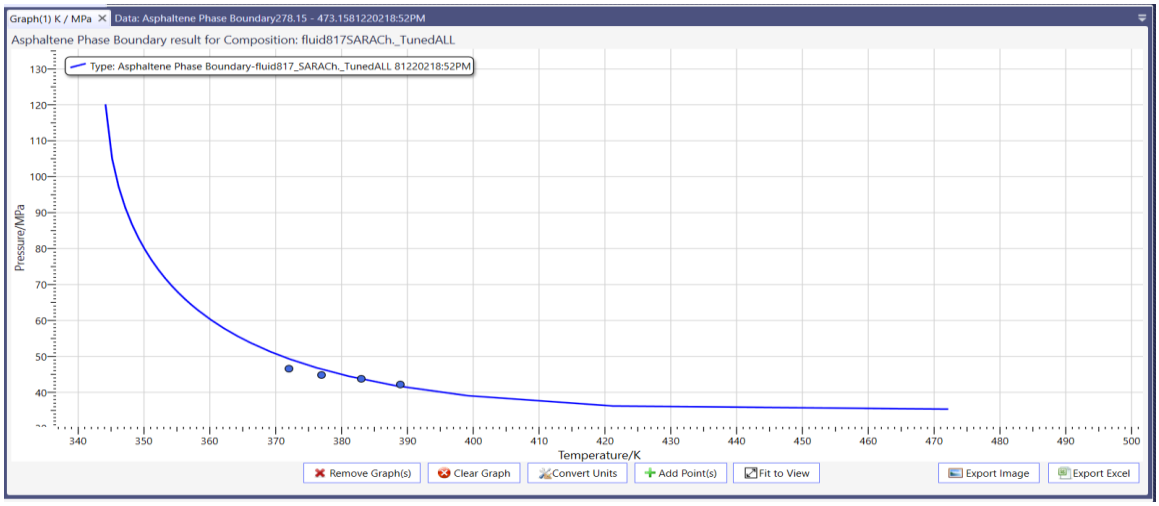


Figure 33 - Asphaltene phase behavior for Fluid 817 (M. A. Fahim, 2007) after tuning the model with experimental AOP data in HydraFLASH, using PC-SAFT model (blue line- upper AOP, blue round circles – experimental measurement of AOP)

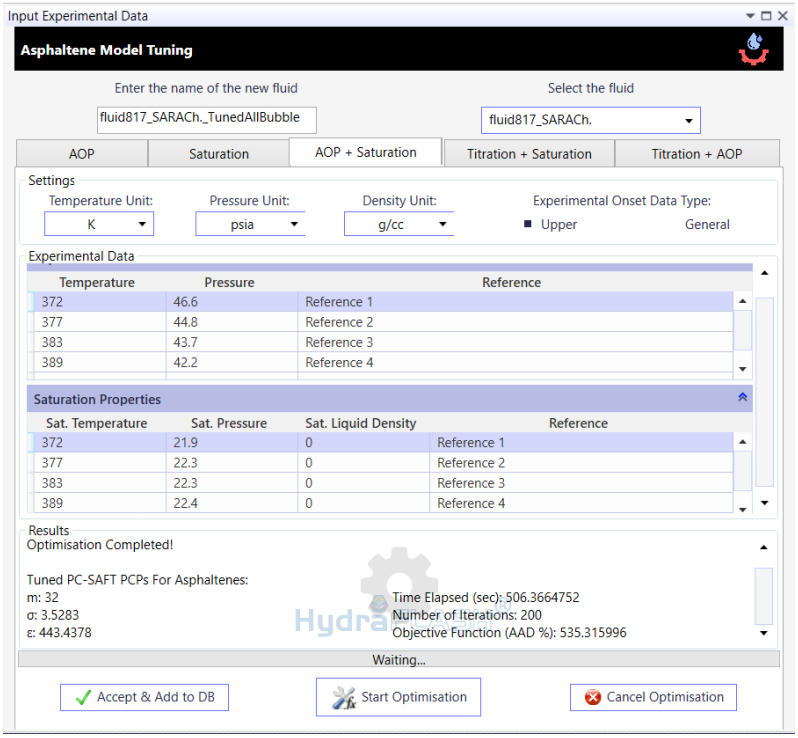


Figure 34 - Tuning the model with AOP and saturation data for fluid 817a in HydraFLASH

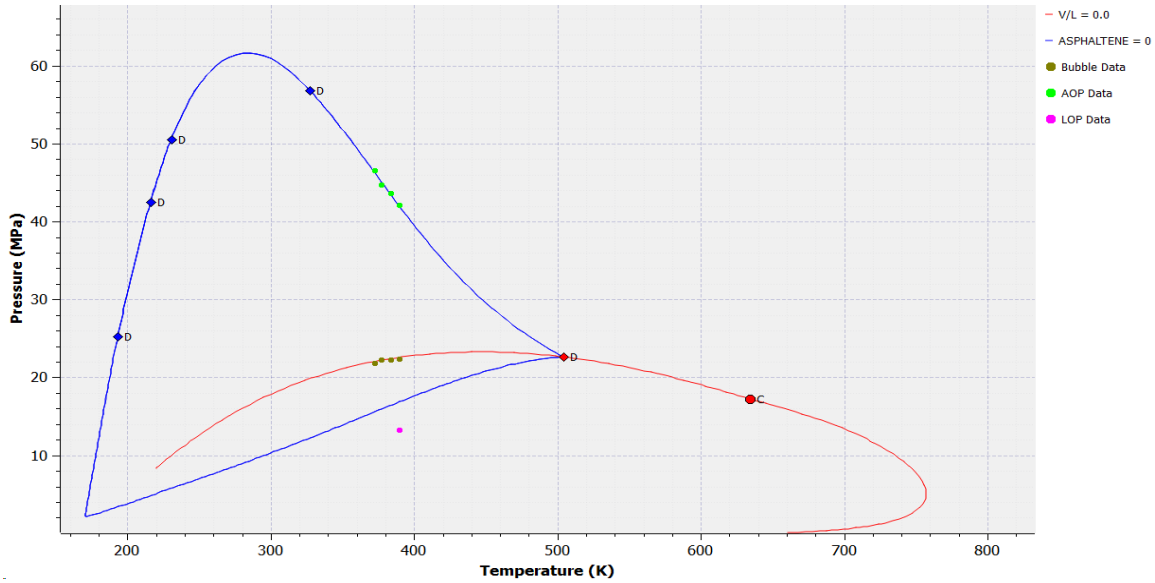


Figure 35 - Asphaltene phase behavior for fluid 817 modeled in Multiflash using CPA model (blue line – prediction of upper and lower AOP boundary when tunning the model with AOP and saturation data, red line – VLE curve after tunning the model with AOP and saturation data)

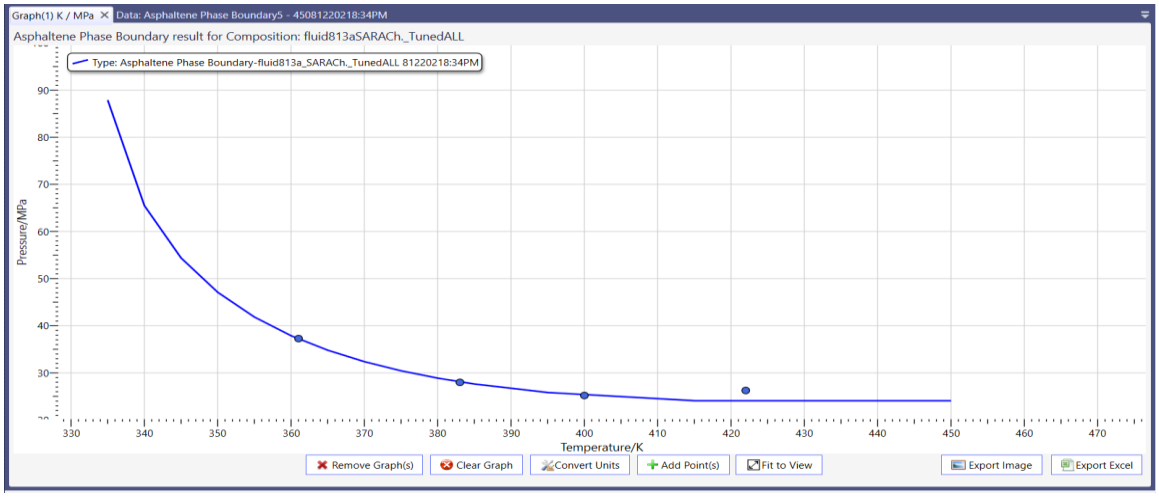


Figure 36 - Asphaltene phase behavior for Fluid 813a (M. A. Fahim, 2007) after tuning the model with experimental AOP data in HydraFLASH, using PC-SAFT model (blue line- upper AOP, blue round circles – experimental measurement of AOP)

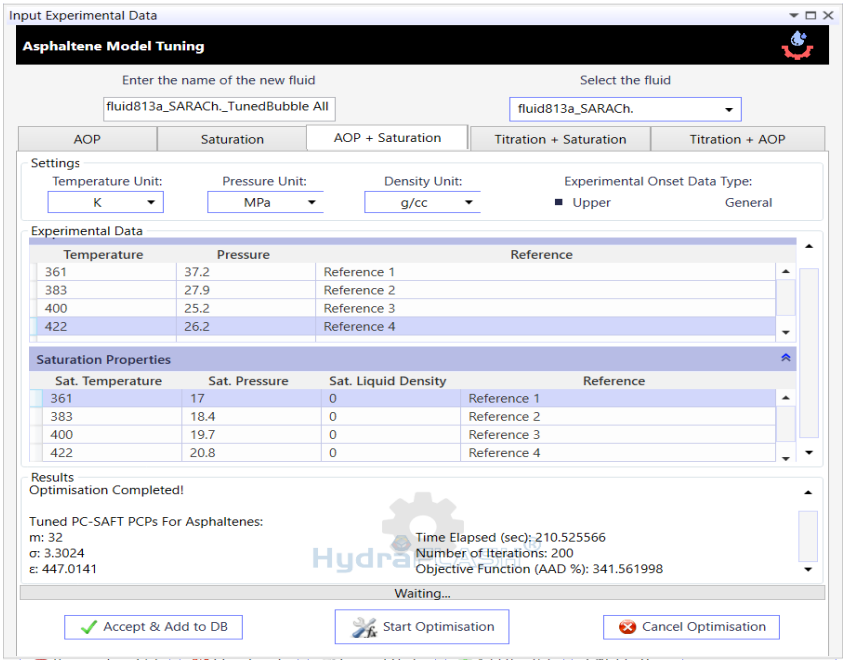


Figure 37 - Tuning the model with AOP and saturation data for fluid 813a in HydraFLASH

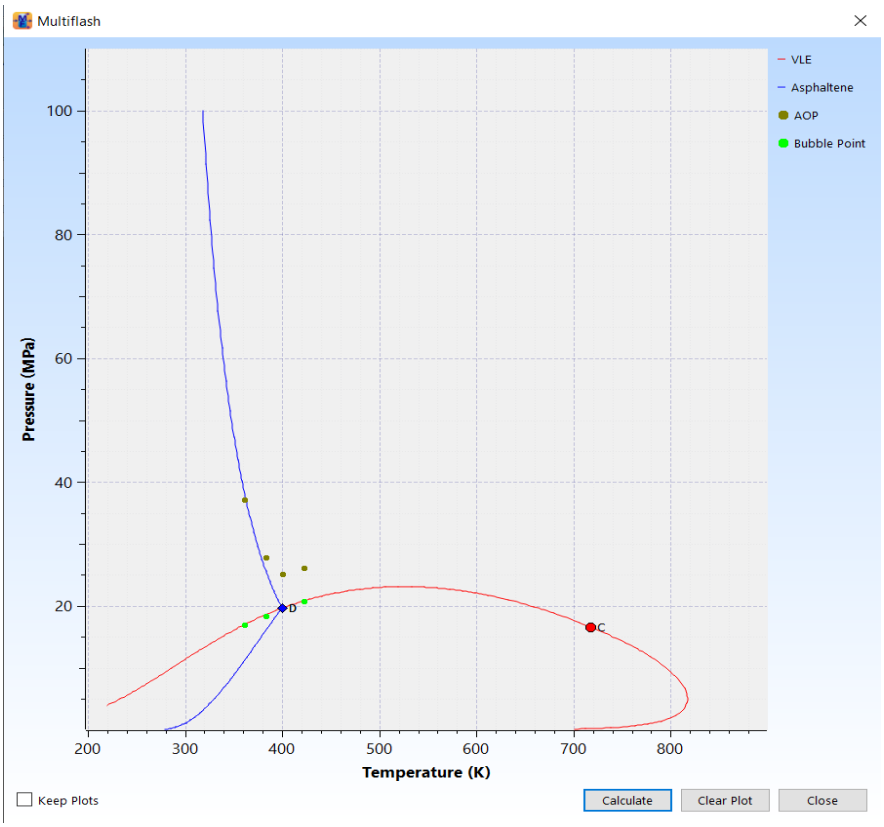


Figure 38 - Asphaltene phase behavior for fluid 813a modeled in Multiflash using CPA model (blue line – prediction of upper and lower AOP boundary when tunning the model with AOP and saturation data, red line – VLE curve after tunning the model with AOP and saturation data)

5.4. LOWER onset

As mentioned before, when pressure falls below the bubble point, gas starts coming out of solution, the composition of oil changes and the content of n-Alkanes decreases in the system, hence solubility of asphaltene in oil composition with less n alkanes will increase. Therefore, asphaltenes will become more soluble and start coming back to solution. Lower asphaltene onset boundary is boundary of conditions below bubble point where last of asphaltene phase is dissolved back into the oil. This boundary is very useful to predict asphaltene behavior in two phase area, on lower pressures and temperatures. These conditions are usually present in wellbore and production facilities, and it is of great importance to know the operating conditions where asphaltenes will not create problems.

Due to the lack of experimental measurements of lower AOP data, only 6 models were successfully run for the purpose of comparing the tuning and modeling of lower asphaltene phase boundary in both software. Both software performed good in tuning the PC-SAFT and CPA models to experimental data and in predicting the lower asphaltene phase behavior. Since there was no difference in performance, the following ability of the models was questioned. As seen before, in both software, it is possible to predict lower asphaltene phase boundary, based on calculations of upper asphaltene phase boundary without tuning the model with experimental lower asphaltene onset pressure. Same stands for upper asphaltene phase boundary – it is possible to predict upper asphaltene phase boundary based on lower asphaltene experimental data. The

question that raised was whether these predictions are reliable and if they are, which model, CPA or PC-SAFT, gave better predictions.

In the following predictions of both upper and lower asphaltene phase boundaries were presented. The following results from both software were compared: prediction based on tuning the model with only upper onset pressure, and prediction based on tuning the model with only lower asphaltene onset pressure. The tuning process in each software was done only based on AOP data, and not saturation and AOP data together. The reason was unreliability of HydraFLASH in tunning the data to saturation properties.

5.3.1 Case 1

Case 1 is an oil for which only one experimental measurement reported for both upper and lower asphaltene onset point. The composition of oil modeled in Case 1 is reported previously in chapter 5.2.1. in table 12. Experimental upper and lower AOP is reported in table 16. Reported bubble pressure at this temperature was 12.6 MPa. Asphaltene model tuning to experimental data for lower AOP was shown in the figure below. Only difference between tuning the model to lower AOP is that in field “experimental data type” the second option “general onset data’ must be chosen (see figure 39).

Table 16 – Experimental upper and lower AOP for Fluid 85

Experimental Upper and lower AOP for fluid 85		
Temperature [K]	Upper AOP [MPa]	Lower AOP [MPa]
386	27.4	6.9

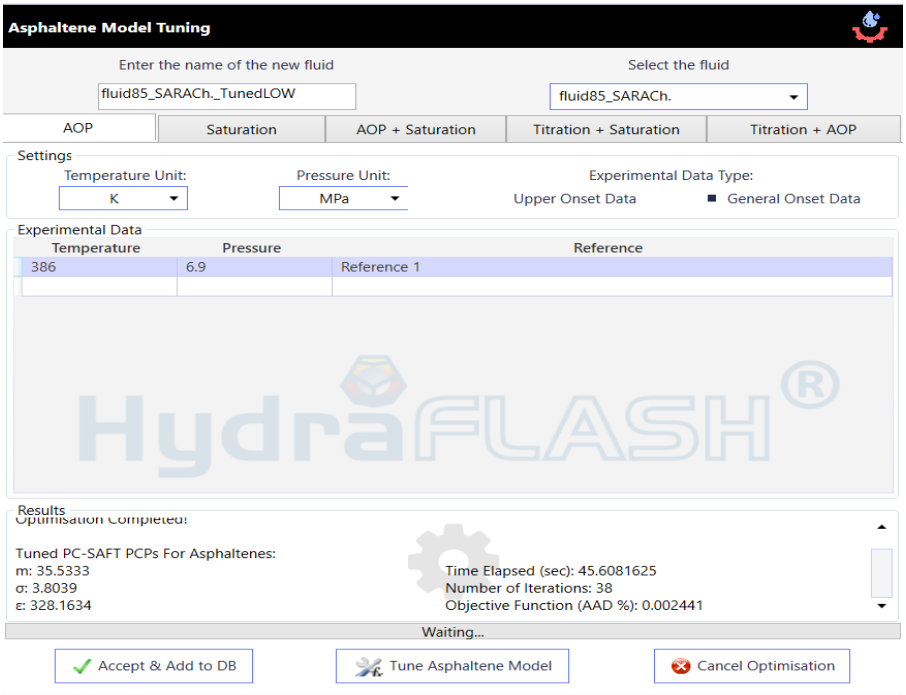


Figure 39 - Tuning process in HydraFLASH when model is being tuned to experimental lower asphaltene onset pressure

In the figure below calculation of lower asphaltene phase boundary when model is tuned to lower AOP and when model is tuned with upper AOP is compared. Blue line represents

prediction of asphaltene lower phase boundary when PC-SAFT model is tuned to lower AOP. It can be noticed that tunning was successful. Blue circle represents experimental data of lower asphaltene onset pressure. Green line, on the other hand represents prediction of asphaltene lower phase boundary when model is tuned with only upper AOP, and then lower asphaltene phase boundary was calculated in the software. It can be noticed that at lower pressure and temperature the difference between predictions is not high, but when we move towards higher pressure and temperatures difference becomes significant. If the temperature of 386 K is observed, green line would predict lower AOP of around 5.5 MPa, instead of 6.9 MPa, that was reported for this temperature.

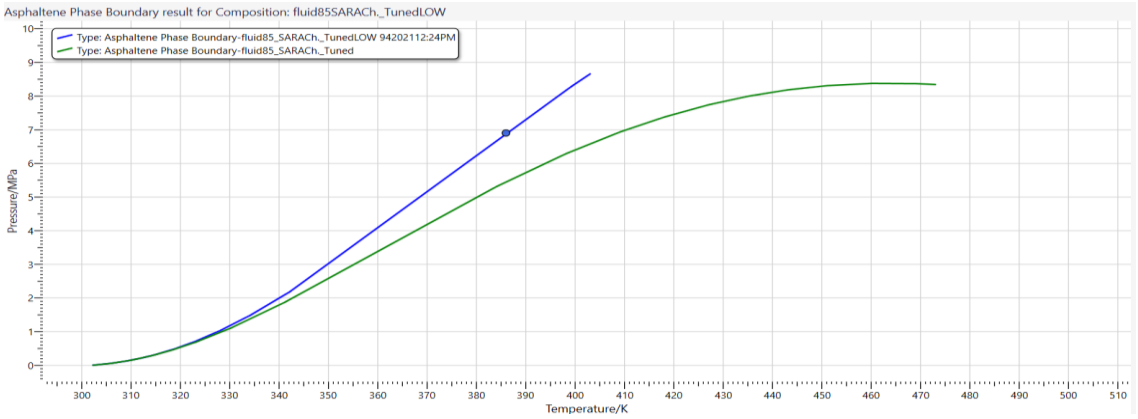


Figure 40 - Comparison of prediction of lower asphaltene phase boundary for fluid 85 in HydraFLASH when model is tuned to lower AOP data (blue line) and when model is tuned to upper AOP data and lower was calculated in software (green line)

The same experiment was repeated, just this time upper asphaltene phase boundary was observed. The results are presented in the figure below. Blue line represents the predictions of asphaltene phase behavior when model is tuned to upper AOP. It can be noticed that tuning was successful. On the other hand, green line represents predictions when tuning was done based on lower AOP, and upper phase boundary was calculated by software. It can be noticed that difference exists between these two predictions and that they are higher than for lower AOP. For the temperature of 386 K, blue line gave good matching with experimental data and reported AOP of 27.4 MPa, while green line predicted AOP of around 22 MPa for the same temperature. This makes difference around 5 MPa, which is almost three times higher than difference for lower AOP between the models.

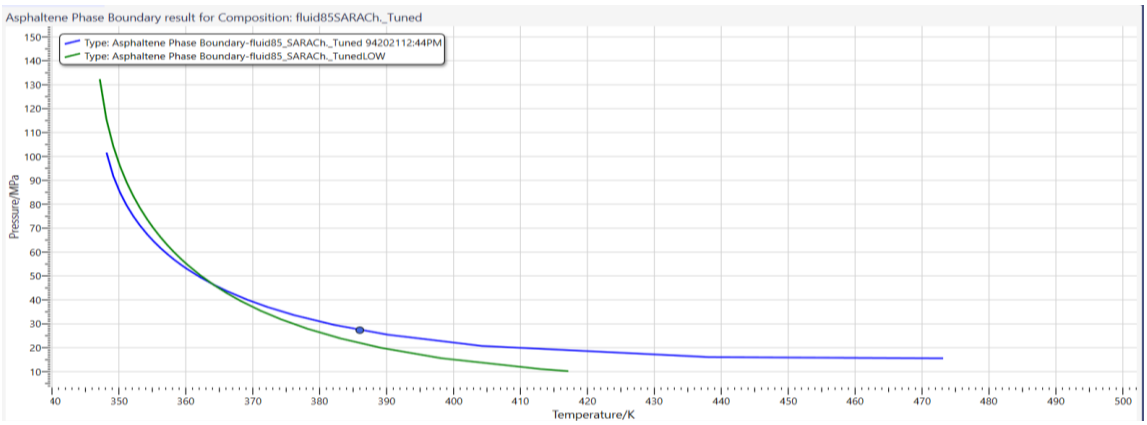


Figure 41 - Comparison of predictions of upper asphaltene phase boundary for fluid 85 in HydraFLASH when model is tuned to upper AOP data (blue line) and when model is tuned to lower AOP data and upper was calculated in software (green line)

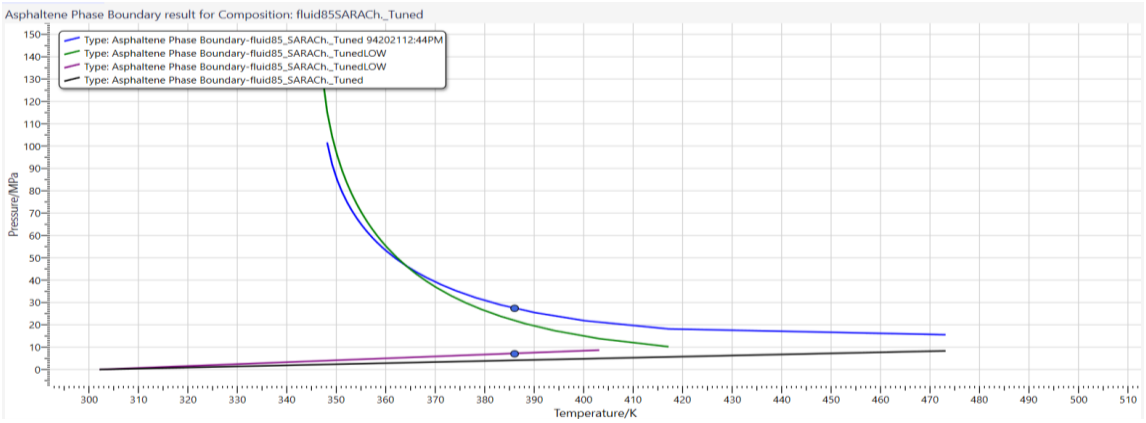


Figure 42 - Predictions of upper and lower asphaltene phase boundaries for fluid 85 in HydraFLASH when model is tuned with upper and with lower experimental AOP (blue lineand black line – upper and lower phase boundary respectively when model is tuned to upper AOP data, green and purple line – upper and lower asphaltene phase boundary respectively when model is tuned to lower AOP data

The same calculations were done in Multiflash and results are presented in the figure 43. In the figure below blue line represents the prediction where model parameters were matched with lower experimental AOP, and green line represents prediction of asphaltene phase behavior when model parameters were tuned to upper experimental AOP. It can be noticed that both predictions are similar and difference increase only with high pressures and lower temperatures.

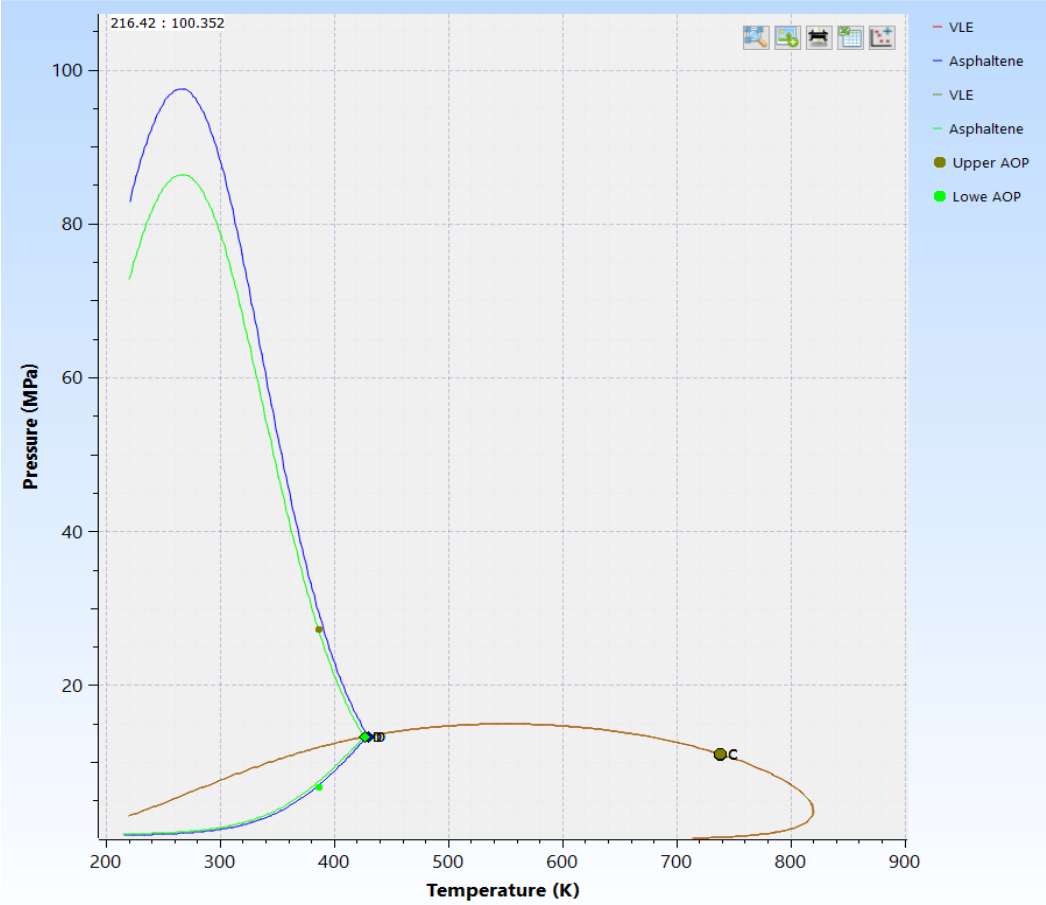


Figure 43 - Predictions of upper and lower asphaltene phase boundaries for fluid 85 in Multiflash when model is tuned with upper (green line) and with lower (blue line) experimental AOP

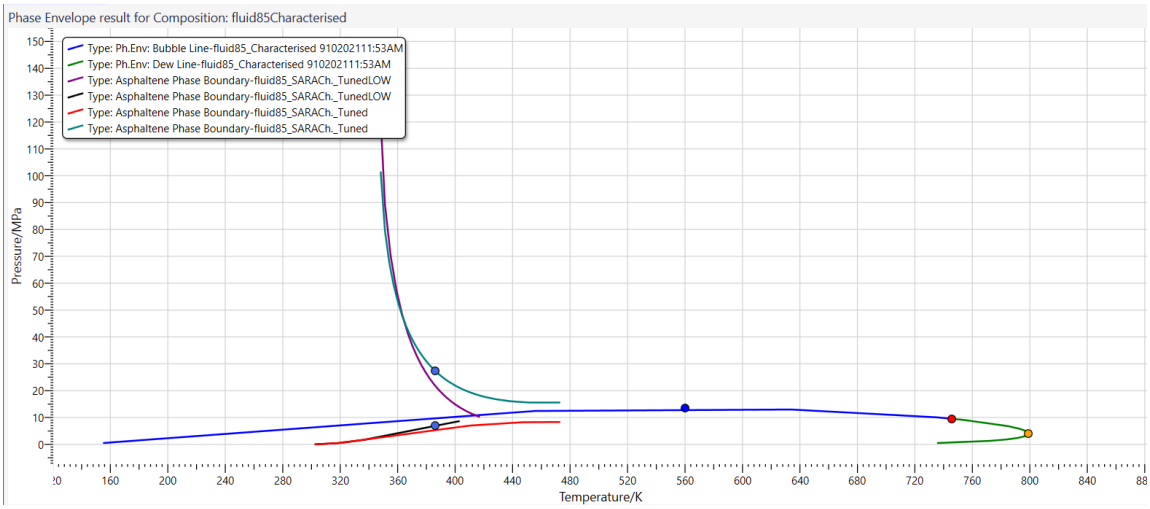


Figure 44– Predictions of asphaltene phase behavior for Fluid 85 in Hydraflash (blue and red line – upper and lower phase boundary respectively when model is tuned to upper AOP data, purple and black line – upper and lower asphaltene phase boundary respectively when model is tuned to lower AOP data, blue and green line- blasé envelope)

From the figures 43 and 44 below it can be noticed that biggest difference between two predictions is around VLE in Hydraflash software. In the results of Multiflash, if can be noticed

that the smallest difference between predictions is around VLE, and it increases only at high pressures and low temperatures. The reliability of the results in software depends on working conditions. If the working conditions and fluid path are close to VLE then Multiflash gave better results regarding the reliability of both tunings, since the difference is the smallest close to VLE.

5.4.2. Case 2

Case 2 is an oil for which there is only one experimental measurement reported for both upper and lower asphaltene onset point. The composition of oil modeled in Case 2 is previously mentioned in chapter 5.1.3. in table 5. The experimental data for upper and lower AOP is in the table 17. Reported bubble pressure at this temperature was 12.9 MPa.

Table 17 – Experimental data of upper and lower AOP for Fluid 83

Experimental Upper and lower AOP for Fluid 83		
Temperature [K]	Upper AOP [MPa]	Lower AOP [MPa]
365	20.1	9.7

In the figure below calculation of lower asphaltene phase boundary when model is tuned to lower AOP and when model is tuned with upper AOP is compared. Blue line represents prediction of asphaltene lower phase boundary when PC-SAFT model is tuned to lower AOP. It can be noticed that tunning was successful. Blue dot represents experimental measurement of lower asphaltene onset pressure. Black line, on the other hand represents prediction of asphaltene lower phase boundary when model is tuned with only upper AOP, and then lower asphaltene phase boundary was calculated in software. It can be noticed that on lower pressure and temperature the difference between predictions is high, but when we move towards higher pressure and temperatures difference becomes significantly smaller. If the temperature of 365 K is observed, black line would predict lower AOP of around 9.5 MPa, instead of 9.7 MPa, that was reported for this temperature. The difference is higher if the observed temperature is for example 310K where the difference between two AOP pressures is 1 MPa.

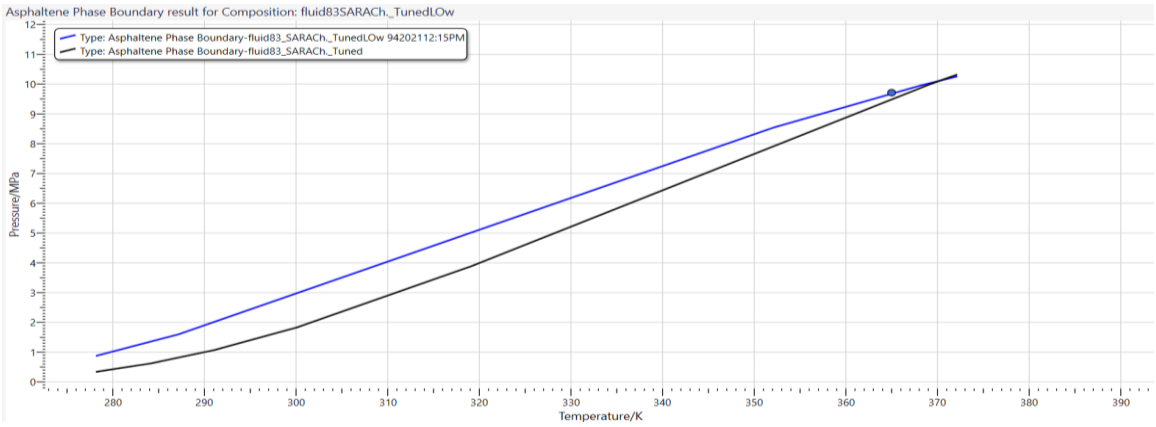


Figure 45 - Comparison of prediction of lower asphaltene phase boundary for fluid 83 in HydraFLASH when model is tuned to lower AOP data (blue line) and when model is tuned to upper AOP data and lower was calculated in software (black line)

The same experiment was repeated, just this time upper asphaltene phase boundary was observed. The results are presented in the figure below. Blue line represents the predictions of asphaltene phase behavior when model is tuned to upper AOP. It can be noticed that tuning was

successful. On the other hand, green line represents predictions when tuning was done based on lower AOP, and upper phase boundary was calculated by software. It can be noticed that difference exists between these two predictions and that they are higher than for lower AOP. For the temperature of 365 K, blue line gave good matching with experimental data and reported AOP of 20.1 MPa, while green line predicted AOP of around 18 MPa for the same temperature. This makes difference around 2 MPa. The difference between two predictions increases towards low temperatures and higher pressures.

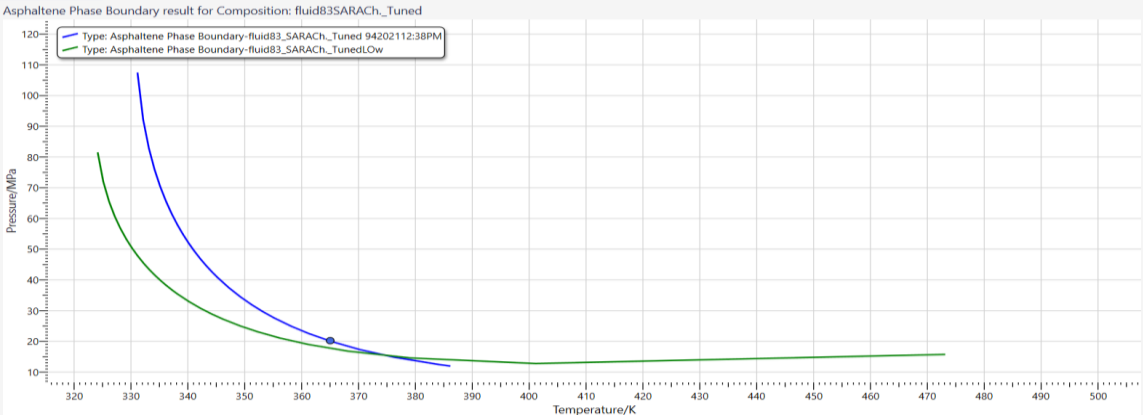


Figure 46 - Comparison of predictions of upper asphaltene phase boundary for fluid 83 in HydraFLASH when model is tuned to upper AOP data (blue line) and when model is tuned to lower AOP data and upper was calculated in software (green line)

Same procedure was repeated in Multiflash. In the figure below blue line represents predictions when model parameters are tuned with lower experimental AOP and green line represents predictions of asphaltene phase behavior when model parameters are tuned with upper experimental AOP. It can be noticed that for temperature of 365 K blue line gives AOP around 30 MPa, instead of 20.1 MPa, which was experimental measurement. On the other hand, green line gives lower AOP of around 12 MPa on the same temperature instead of 9.5 MPa, which was measured AOP. It can be noticed that difference between predictions of upper asphaltene phase boundary is higher than between predictions of lower asphaltene phase boundary.

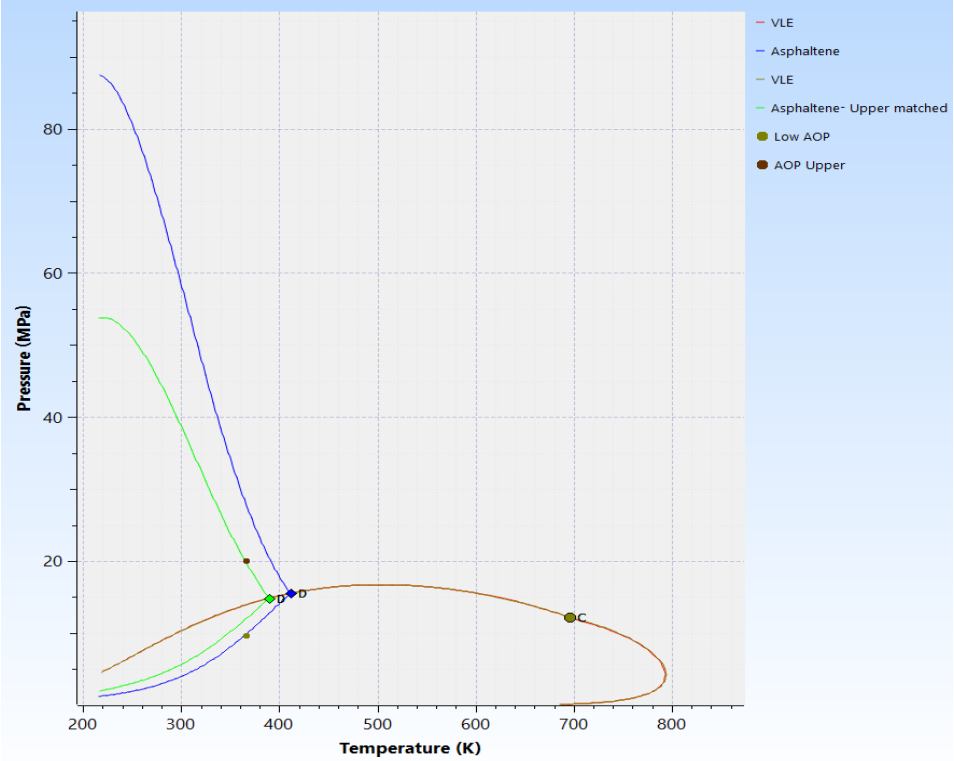


Figure 47 - Predictions of upper and lower asphaltene phase boundaries for fluid 83 in Multiflash when model is tuned with upper (green line) and with lower (blue line) experimental AOP

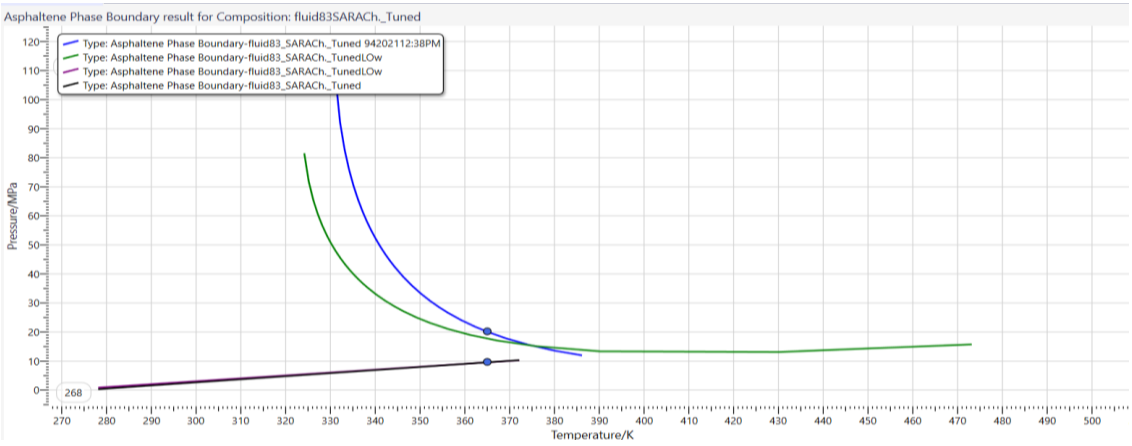


Figure 48 - Predictions of upper and lower asphaltene phase boundaries for fluid 83 in HydraFLASH when model is tuned with upper and with lower experimental AOP (blue lineand black line – upper and lower phase boundary respectively when model is tuned to upper AOP data, green and purple line – upper and lower asphaltene phase boundary respectively when model is tuned to lower AOP data

From the figures above it can be noticed that biggest difference between two models is around VLE in HydraFLASH software. In the results of Multiflash, if can be noticed that the smallest difference between models is around VLE, and it increases only at high pressures and low temperatures.

5.4.3. Case 3

Case 3 is an oil for which HydraFLASH did not match Bubble point good and the effect on position of asphaltene lower phase boundary was investigated. Composition of fluid 86 (M.A.Fahim, 2007) is presented in the table below. Experimental AOP, lower and upper was reported on temperature of 361 K.

Table 18 – Composition of Fluid 86

Components	Oil Composition
H_2S	0
N_2	0.8
CO_2	0.05
C_1	51.02
C_2	8.09
C_3	6.02
iC_4	3.97
iC_5	3.21
C_6	2.67
C_7	24.17

Table 19 – Experimental upper and lower AOP for Fluid 86

Experimental Upper and lower AOP for Fluid 86			
Temperature [K]	Upper AOP [MPa]	Lower AOP [MPa]	Bubble Pressure [MPa]
361	36.4	26.4	29.4

From the figure below it can be seen that due to bad tuning of model parameters to saturation properties phase envelope is below lower asphaltene phase boundary.

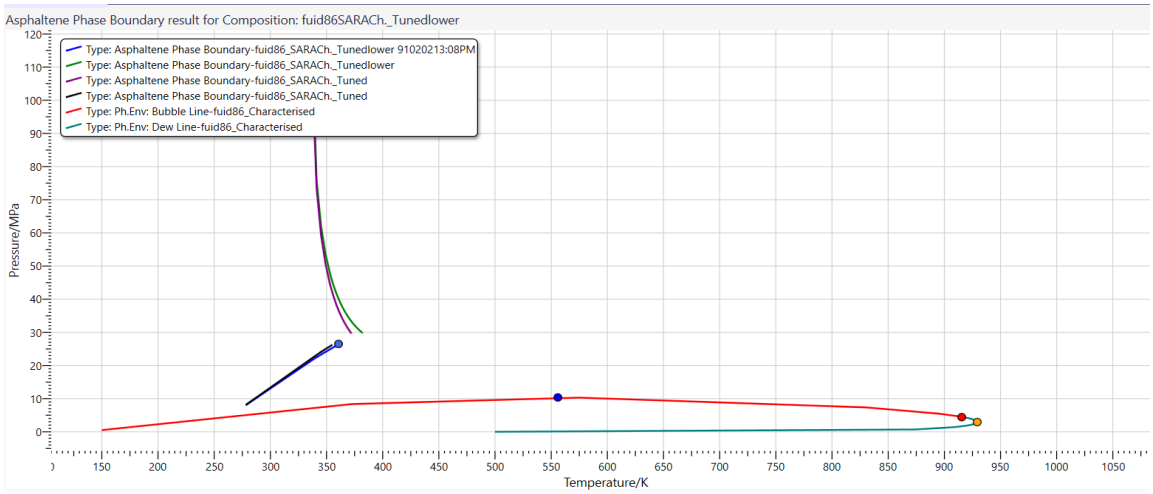


Figure 49 – Asphaltene phase behavior for Fluid 86 modeled in HydraFLASH

Based on the results that were obtained from both software it can be concluded that out of 6 successful models Hydraflash performed better in 5 and Multiflash performed better in only one case. When comparing the quality in performance the difference between predictions of case where model parameters were matched with lower AOP experimental data and case where model parameters were matched with upper AOP experimental data was compared. For better explanation of the conclusions obtained two cases were observed:

1. Case 1 is when model parameters were tuned to lower experimental AOP data and upper and lower asphaltene phase boundaries were calculated by software
2. Case 2 is when model parameters were tuned with upper experimental AOP data and upper and lower phase boundaries were calculated by software

From 6 oil compositions that were modeled in both software it was concluded that case 2 gives better results in predictions of phase boundaries predictions than case 1. When software successfully matched model parameters to experimental data, the phase boundary, lower or upper, will always be more accurate if the model was matched with appropriate data. For example: if model parameters are matched with upper AOP experimental data, and the matching was successful then predictions of upper asphaltene phase boundary will be way better then predictions of lower asphaltene phase boundary that was calculated based on the same matching (case 2 mentioned above). Same stands for the case where the model parameters are matched with lower AOP experimental data – lower asphaltene phase boundary will be predicted more accurate than upper asphaltene phase boundary (case 1 mentioned above).

When these two cases were compared it was concluded that case 2 will make much smaller error in prediction the lower asphaltene phase boundary then case 1 when predicting upper phase boundary. As a conclusion for predicting the phase behavior of asphaltenes it is much better to have experimental measurement of upper asphaltene onset pressure and calculate lower phase boundary based on it, then to have experimental measurement of lower AOP and calculate upper phase boundary based on it.

In the figure below this theory is presented. The black and blue line represent case 2, where model was tuned with upper asphaltene onset pressure experimental data, and purple and green line represent case 1, where model parameters were tuned with lower asphaltene onset pressure experimental data. It can be noticed that difference in lower asphaltene phase boundaries

is significantly smaller than difference between upper asphaltene phase boundaries. This concludes that with having upper AOP experimental data asphaltene phase behavior can be predicted more accurate.

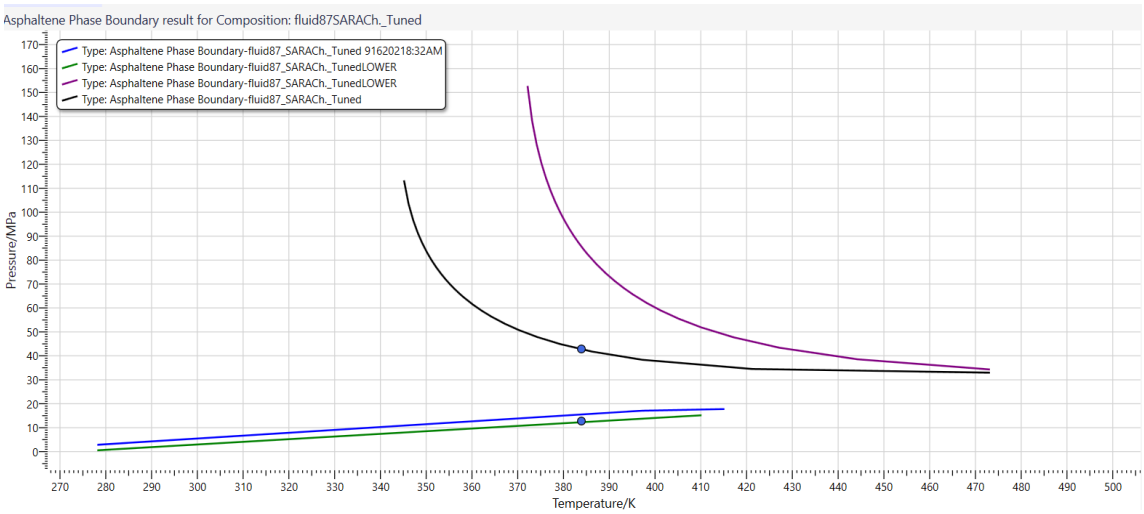


Figure 50 - Predictions of upper and lower asphaltene phase boundaries for fluid 87 in HydraFLASH when model is tuned with upper and with lower experimental AOP (black lineand blue line – upper and lower phase boundary respectively when model is tuned to upper AOP data, purple and green line – upper and lower asphaltene phase boundary respectively when model is tuned to lower AOP data

6. Conclusion

Modeling asphaltene phase behavior is a complex problem and making a clear judgment on which model, PC-SAFT or CPA, performed better in which conditions requires more investigation. What was done in this thesis is presentation and discussion of differences between PC-SAFT and CPA models' predictions of asphaltene phase behavior. The major difference between in performance was seen in predictions of asphaltene phase behavior boundary, where CPA model gave very unusual results. The effect of tuning the model parameters with saturation properties was also compared. The reliability of both software was tested and overall both models had their strengths and weaknesses Recommendation for future work would be solving the problems that were mentioned in chapter 5: resolving the issue of CPA model predictions that gave peak in asphaltene phase envelope, resolving the problem of tuning PC-SAFT model with saturation properties, and finally gathering more data from gas injection, titration and depressurization AOP measurements. That study could make a clear judgement on which model is better for modeling asphaltene phase behaviors and under which conditions.

7. References

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