

Modelling the Asphaltene Precipitation of Live Oils in the Symmetry* Process Software Platform

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Introduction

Heavy oils are rich in asphaltenes; the heaviest and most polar fraction of a crude oil. Asphaltenes are generally defined as a solubility class of materials that are insoluble in n-alkanes like n-pentane or n-heptane but soluble in aromatics solvents such as toluene.

Asphaltenes can precipitate along the whole oil production process due to changes in temperature, pressure and composition causing operational problems. During oil production, asphaltenes can block the porous channels of the reservoir rock making oil mobility very difficult. In the transportation process, the asphaltene precipitation makes pumping challenging due to a viscosity increment and at the surface, the oil needs to be blended with diluents to lower its viscosity. In refinery operations asphaltenes can plug refinery equipment increasing the frequency of maintenance intervention procedures.

One of the historical challenges in phase behavior simulation is the prediction of the conditions at which asphaltene precipitation occurs, the amount of precipitate, and the properties of the asphaltene-rich phase. To address these issues, the Symmetry process platform has recently added the **Asphaltene Precipitation for Live Oils** to the list of characterization options available in the Oil Source unit operation, this option is backed up by the Symmetry process platform's own PIONA Molecular based characterization procedure [1].

The characterization is complemented with Asphaltene Onset Pressure and Asphaltene precipitated fraction calculations at given conditions. The calculations can help in the monitoring process of asphaltene precipitation in a flowsheet.

The objective of this communication is to offer a walkthrough of the characterization process of a live oil that contains asphaltenes that may precipitate during oil production and, to highlight tools available in the Symmetry process platform to monitor and detect precipitated asphaltenes. This will be done with the help of an example based on a reservoir fluid described in open literature.

Asphaltene Precipitation for Live Oils

To start the characterization of a live oil or reservoir fluid with asphaltene content, we need the following data set: light ends analysis and Stock Tank properties (SARA distribution in wt %, Oil density, molecular weight (optional) and Gas to Oil ratio). These properties are enough to obtain asphaltene precipitation calculations since they provide the basis of internal correlations that arrange the PIONA slate components in a way that flash calculations can produce an asphaltene-like phase.

If experimental Saturation and Asphaltene Onset Pressures are available, they can be used to tune parameters and match calculated phase boundary pressures.

Gonzalez et al. [2] studied the asphaltene precipitation phase behavior of live oil samples, the following tables show the reported characterization data for one of them that include: stock tank oil properties, light ends analysis, and phase boundaries conditions. This reservoir fluid will be used to exemplify the characterization and tuning procedure for asphaltene precipitation.

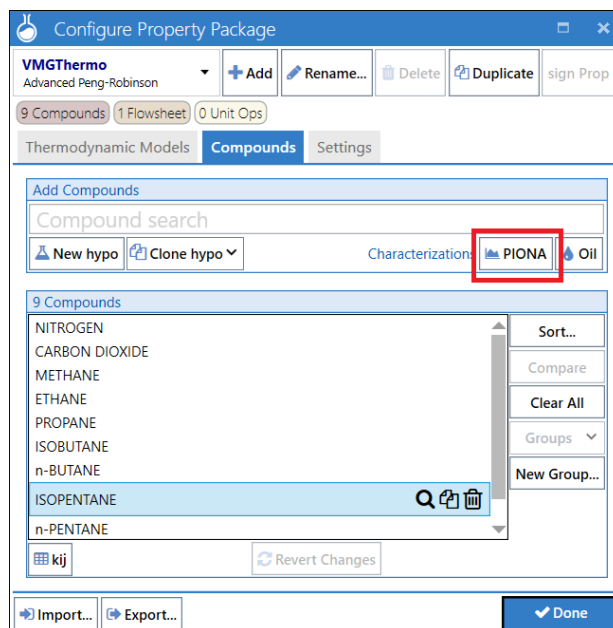
STOCK TANK OIL PROPERTIES	
Density (kg/m ³) at 60F	919
GOR (Sm ³ / m ³)	100.63
Saturates (wt%)	39.36
Aromatics (wt%)	36.04
Resins (wt%)	9.04
Asphaltenes (wt%)	15.56

Light Ends Composition	
Component	Mass %
NITROGEN	0.078
CARBON DIOXIDE	0.058
METHANE	4.318
ETHANE	2.005
PROPANE	2.266
ISOBUTANE	0
n-BUTANE	0.537
ISOPENTANE	0
n-PENTANE	2.066

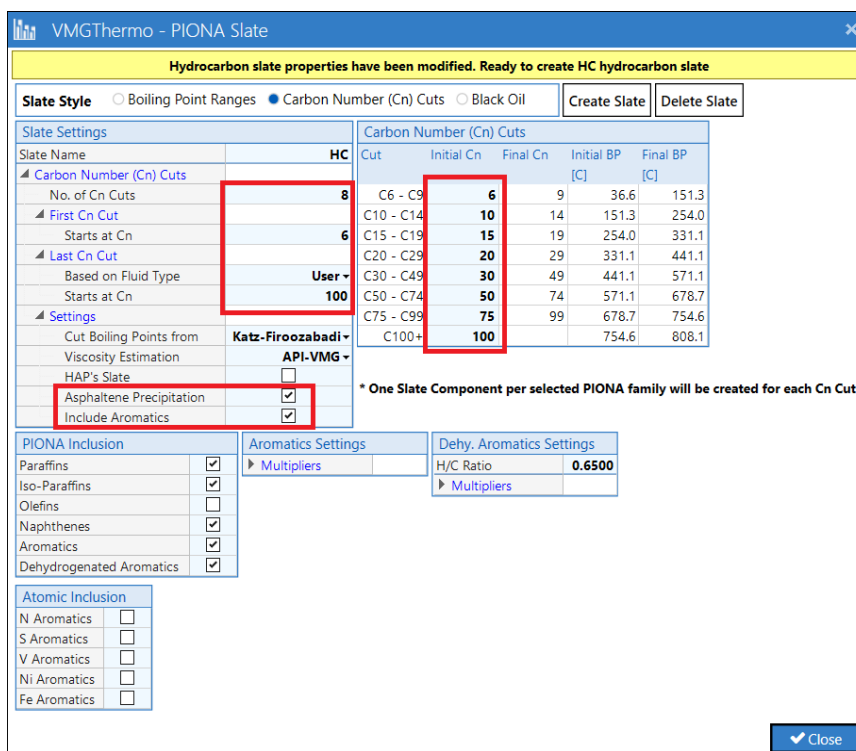
SATURATION PRESSURES	
Temperature (°C)	Pressure (kPa)
26.67	11718
31.11	12063
37.78	12752
65.56	14668
97.78	16681

Asphaltene Onset Pressure	
Temperature (°C)	Pressure (kPa)
27	59279
31.11	55143
38	46182
65	34809
98	31707

As mentioned above, the asphaltene precipitation procedure in the Symmetry process platform is based on components created from its PIONA Molecular based characterization; a key part in the characterization procedure is the setup of the PIONA components slate. Let's begin the process by opening a new case using the **Advanced Peng-Robinson** property package with the following pure light end components defined in the previous tables:



Then we can open the **PIONA Slate** environment by clicking on the PIONA button from the previous window. In the PIONA Slate window enter the following values using the *Carbon Number (Cn) Cuts* Slate Style. Note that the *Asphaltene Precipitation* and *Include Aromatics* boxes are checked in order to create an extended list of aromatic and dehydrogenated aromatic components which will represent the Asphaltene-like components. When creating the PIONA Slate, it is recommended to use the Carbon Number (Cn) Cuts Style as this style allows the inclusion of heavy Aromatic and Dehydrogenated aromatic components that can act as asphaltene-like compounds.



The asphaltene-like components are Aromatic and Dehydrogenated Aromatic compounds with large Carbon Numbers ($C_n > 100$). The equation of state (EOS) binary interaction parameters for these components with other non-asphaltene hydrocarbons have been tuned to allow the precipitation of a heavy hydrocarbon phase rich in asphaltene-like components. The EOS binary interaction parameters have been tuned for the following Symmetry process platform's property packages: *Advanced Peng-Robinson*, *Advanced Peng-Robinson for Natural Gas*, *Advanced Peng-Robinson for Natural Gas 2* and *Refinery-APR*.

Once the PIONA Slate window is set up click on the Create Slate button to add the PIONA based components to the property package. Now, we are ready to start the characterization procedure.

Go to the flowsheeting environment, change the Unit Set to *SI* and add an Oil Source unit operation. Open the unit operation and select *Oil / Refinery* as the Application type and check the *Asphaltene Precipitation (Live Oil)* box. Observe that the Cut Ranges option is automatically enabled, this is because the Asphaltene Precipitation characterization will be based on cut ranges that will be defined by the SARA Distribution, light ends composition and the Yield and Density factors from the Settings tab.

The screenshot displays the configuration window for an Oil Source unit operation. Key settings include:

- Application:** Oil / Refinery (selected)
- Summary:** Yields (Cut Range) and Saturation / Asphaltene Onset P (selected)
- Laboratory Analyses:** Cut Ranges and Asphaltene Precipitation (Live Oil) (checked)
- Bulk Experimental Variables:**
 - Stock Tank Oil Density [kg/m3]: 1.0000
 - Stock Tank Oil MW: 1.00
 - Gas to Oil Ratio (GOR) [Sm3/m3]: 1.00
- Options:**
 - Reference Conditions:
 - Liq. Ref. T [C]: 15.6
 - Liq. Ref. P [kPa]: 101.33
- SARA Distrib. (Stock Tank Oil):**
 - Saturates (mass) [%]
 - Aromatics (mass) [%]
 - Resins (mass) [%]
 - Asphaltenes (mass) [%]

Now enter the SARA distribution information from the tables above.

Missing Live Oil Light Ends composition. Please enter data in Yields (Cut Range) tab

Name: OilFeed1

Application: Tight Fluids Oil / Refinery Deasphalting Black Oil

Summary | Yields (Cut Range) | Saturation / Asphaltene Onset P | Settings | Equilibrium Results | Notes | Help

Laboratory Analyses

- Cut Ranges
- Inputs
- PIONA Distribution
- Atomic Inclusion
- Properties
- Asphaltene Precipitation (Live Oil)

Bulk Experimental Variables

Names	Active	Specified	Calculated	Scale
Stock Tank Oil Density [kg/m ³]	<input type="checkbox"/>			1.0000
Stock Tank Oil MW	<input type="checkbox"/>			1.00
Gas to Oil Ratio (GOR) [Sm ³ /m ³]	<input type="checkbox"/>			1.00

Options

- Reference Conditions
 - Source: Global
 - Liq. Ref. T [C]: 15.6
 - Liq. Ref. P [kPa]: 101.33
 - Asphaltene Calculations:
- SARA Distrib. (Stock Tank Oil)
 - Saturates (mass) [%]: 39.36
 - Aromatics (mass) [%]: 36.04
 - Resins (mass) [%]: 9.04
 - Asphaltenes (mass) [%]: 15.56

Material

PortName	Out
Is Recycle Port	<input type="checkbox"/>
Connected Stream/Unit Op	
VapFrac	
T [C]	
P [kPa]	
Mole Flow [kmol/h]	
Mass Flow [kg/h]	
Volume Flow [m ³ /h]	
Std In Volume Flow [m ³ /h]	

Regress Parameters | Custom Regression Case... Ignored

Note that the status bar is now asking for the Light Ends composition; to add it go to the Yields (Cut Range) tab and enter it in the corresponding frame.

Solved (Material port is not Solved. Missing specifications)

Name: OilFeed1

Application: Tight Fluids Oil / Refinery Deasphalting Black Oil

Summary | Yields (Cut Range) | Saturation / Asphaltene Onset P | Settings | Equilibrium Results | Notes | Help

Options

- Cuts: 5
- Yield Basis: Mass
- Cut Ranges IBP [C]: -252.8
- Cut Ranges EBP [C]: 1443.4
- Light Ends Analysis:
- Light Ends Basis: Mass
- Incl. Light Ends in Cuts:
- Asphaltenes Content:
- Spec. Asph. Mass Cont. [%]: 13.80
- Calc. Asph. Mass Cont. [%]: 13.80
- Asph. A/Adh Mass Ratio: 2.70

Light Ends

Specify	Component	BP [C]	Cn	Mass [%]
<input checked="" type="checkbox"/>	NITROGEN	-195.8		0.08
<input checked="" type="checkbox"/>	CARBON DIOXIDE	-87.5		0.06
<input checked="" type="checkbox"/>	METHANE	-161.5	C1	4.32
<input checked="" type="checkbox"/>	ETHANE	-88.6	C2	2.01
<input checked="" type="checkbox"/>	PROPANE	-42.0	C3	2.27
<input checked="" type="checkbox"/>	ISOBUTANE	-11.7	C4	0.00
<input checked="" type="checkbox"/>	n-BUTANE	-0.5	C4	0.54
<input checked="" type="checkbox"/>	ISOPENTANE	27.8	C5	0.00
<input checked="" type="checkbox"/>	n-PENTANE	36.1	C5	2.07

Cut Range Yields

Cut Names	Start T [C]	End T [C]	Yield Spec. [%]	Yields Calc. [%]	Cum. Yield [%]
Light Ends	-252.8	145.0	34.22	34.22	34.22
Cut_1	145.0	285.0	15.37	15.37	49.59
Cut_2	285.0	550.0	21.56	21.56	71.15
Cut_3	550.0	764.0	15.06	15.06	86.20
Asphaltenes	764.0	1444.4	13.80	13.80	100.00

Yield Spec [%]

Legend: Specified (Blue), Calculated (Orange)

Chart X-axis: Cut Names (Light Ends, Cut_1, Cut_2, Cut_3, Asphaltenes)

Equation: $X = -0.19925, Y = 26.3158$

Regress Parameters | Custom Regression Case... Ignored

Now, observe that five Cut Ranges have been automatically defined (Light Ends, Cut_1, Cut_2, Cut_3 and Asphaltenes), the last cut represents the asphaltene fraction and its yield has been normalized based on the stock tank asphaltene content and light ends information.

We now need to tune some parameters to find the best slate composition that matches the experimental asphaltene precipitation data. Go back to the Summary tab and enter the Stock Tank properties and define the following P, T and Mole Flow in the Material port: 60 C, 101.325 kPa and 1 kmol/h.

The screenshot shows the 'OilFeed1 (Oil Source)' software interface. The 'Summary' tab is active, displaying various parameters and tables. The 'Bulk Experimental Variables' table is highlighted with a red box around the 'Specified' column.

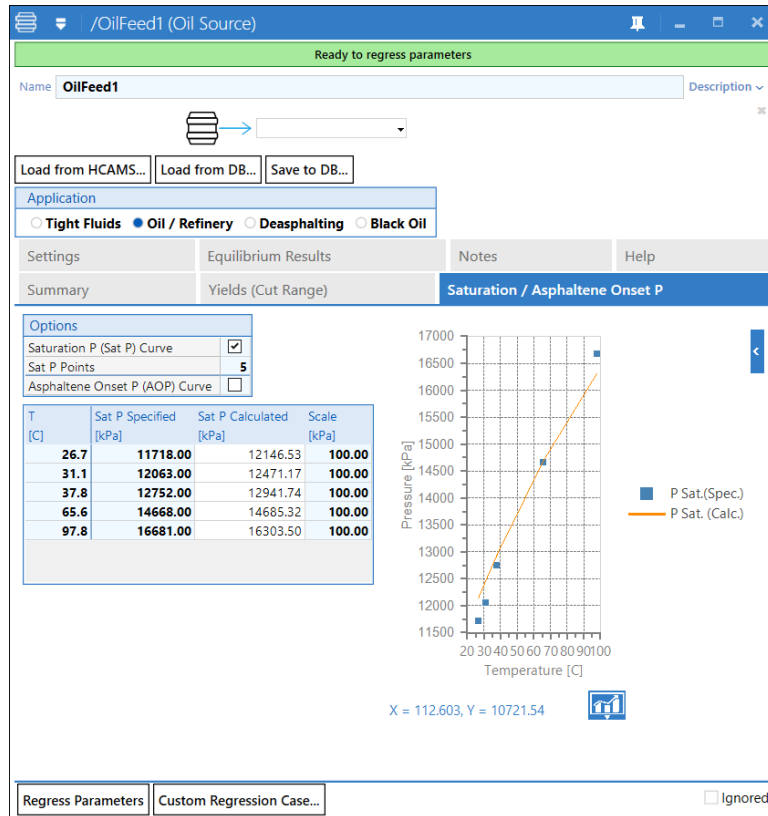
Names	Active	Specified	Calculated	Scale
Stock Tank Oil Density [kg/m ³]	<input checked="" type="checkbox"/>	919.0000	887.3593	1.0000
Stock Tank Oil MW	<input type="checkbox"/>		193.82	1.00
Gas to Oil Ratio (GOR) [Sm ³ /m ³]	<input checked="" type="checkbox"/>	100.63	96.59	1.00

Reference Conditions	Value
Source	Global
Liq. Ref. T [C]	15.6
Liq. Ref. P [kPa]	101.33
Asphaltene Calculations	<input type="checkbox"/>

SARA Distrib. (Stock Tank Oil)	
Saturates (mass) [%]	39.36
Aromatics (mass) [%]	36.04
Resins (mass) [%]	9.04
Asphaltenes (mass) [%]	15.56

Material	
PortName	Out
Is Recycle Port	<input type="checkbox"/>
Connected Stream/Unit Op	
VapFrac	0.56704
T [C]	60.0
P [kPa]	101.33
Mole Flow [kmol/h]	1.00
Mass Flow [kg/h]	114.62
Volume Flow [m ³ /h]	15.485
Std Liq Volume Flow [m ³ /h]	0.147
Std Gas Volume Flow [Sm ³ /d]	5.6857E+2

The next step is to add the vapor pressure data. Go to the **Saturation / Asphaltene Onset P** tab and enter the Saturation Pressure data from Gonzalez et al. [2]:



The Saturation pressure data is calculated based on the defined cut ranges which depend on the *Yield* and *Density Regression Parameters* from the **Settings** tab. To match the data, we need to tune these parameters and to accelerate the solution set the *Max. Iteration* parameter to 50 in the **Settings** tab, then click on the *Regress Parameters* button to run a regression that will match the Saturation Pressure and Stock tank properties by manipulating the Regression Parameters.

Ready to regress parameters

Name: OilFeed1

Application: Tight Fluids Oil / Refinery Deasphalting Black Oil

Settings | Equilibrium Results | Notes | Help

Load Parameters for: Asphaltene

Main Settings

Cut Group Delta T [C]	20.00
PIONA Distrib. Delta T [C]	405.00
Regression	
Max. Iterations	50
Regression Tolerance	0.1000
Optimization Method	Nelder Mead
Obj. Function Type	Least Squares

PIONA Family Inclusion

Paraffins	<input checked="" type="checkbox"/>
Iso-Paraffins	<input checked="" type="checkbox"/>
Olefins	<input type="checkbox"/>
Naphthenes	<input checked="" type="checkbox"/>
Aromatics	<input checked="" type="checkbox"/>

Regressed Parameters

Split P	2.00
Split I	2.00
Split O	0.00
Split N	1.50
Split A	1.00
Split Adh	0.3500
Yield Factor 1	2.30
Yield Factor 2	1.49
Density Factor 1	1.00
Density Factor 2	715.00
Alpha (Asp)	3.00
Eta (Asp)	1000.00
MW (Asp)	2500.00

Regress Parameters | Custom Regression Case... Ignored

Once it is done (it may take a few minutes depending on the computer) observe the new results:

Ready to regress parameters

Name: OilFeed1

Application: Tight Fluids Oil / Refinery Deasphalting Black Oil

Settings | Equilibrium Results | Notes | Help

Summary | Yields (Cut Range) | Saturation / Asphaltene Onset P

Laboratory Analyses

Cut Ranges	<input checked="" type="checkbox"/>
Inputs	<input type="checkbox"/>
PIONA Distribution	<input type="checkbox"/>
Atomic Inclusion	<input type="checkbox"/>
Properties	<input checked="" type="checkbox"/>
Asphaltene Precipitation (Live Oil)	<input checked="" type="checkbox"/>

Bulk Experimental Variables

Names	Active	Specified	Calculated	Scale
Stock Tank Oil Density [kg/m3]	<input checked="" type="checkbox"/>	919.0000	905.5467	1.0000
Stock Tank Oil MW	<input type="checkbox"/>		174.91	1.00
Gas to Oil Ratio (GOR) [Sm3/m3]	<input checked="" type="checkbox"/>	100.63	98.85	1.00

Options

Reference Conditions	
Source	Global
Liq. Ref. T [C]	15.6
Liq. Ref. P [kPa]	101.33
Asphaltene Calculations	<input type="checkbox"/>

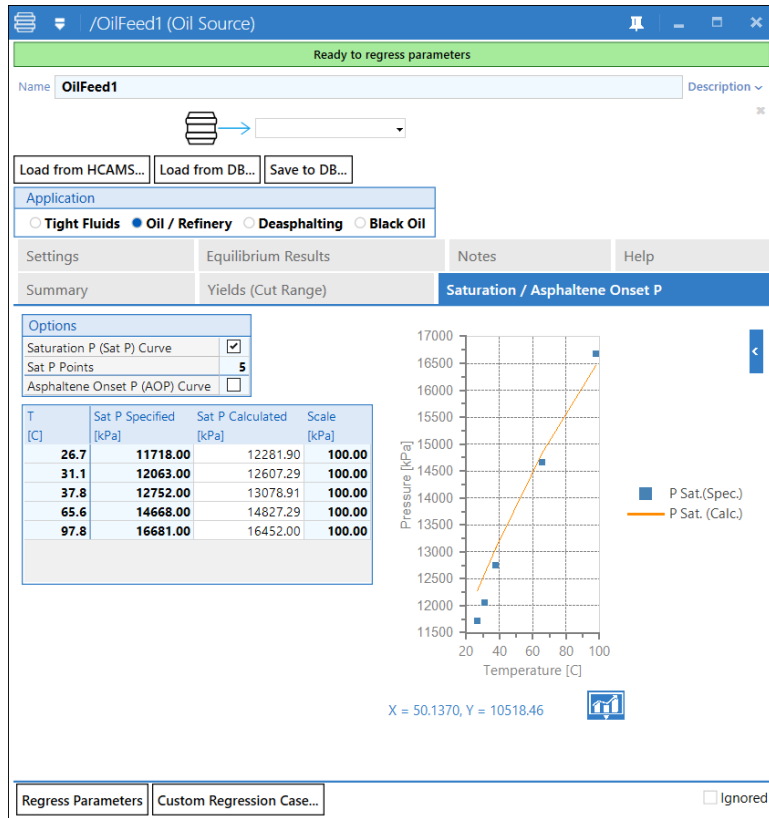
SARA Distrib. (Stock Tank Oil)

Saturates (mass) [%]	39.36
Aromatics (mass) [%]	36.04
Resins (mass) [%]	9.04
Asphaltenes (mass) [%]	15.56

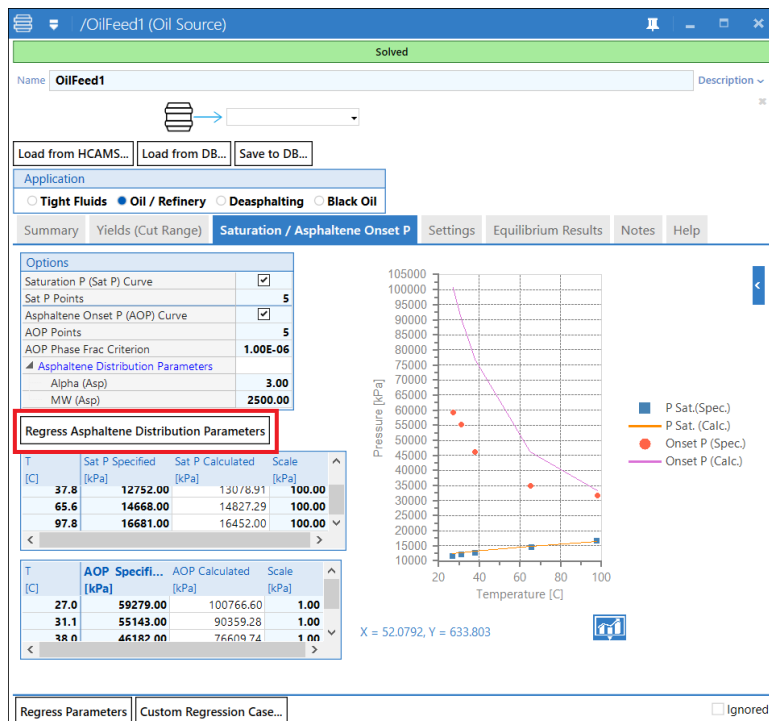
Material

PortName	Out
Is Recycle Port	<input type="checkbox"/>
Connected Stream/Unit Op	
VapFrac	0.55245
T [C]	60.0
P [kPa]	101.33
Mole Flow [kmol/h]	1.00
Mass Flow [kg/h]	108.38
Volume Flow [m3/h]	15.070
Std Liq Volume Flow [m3/h]	0.137
Std Gas Volume Flow [Sm3/d]	5.6857E+2

Regress Parameters | Custom Regression Case... Ignored

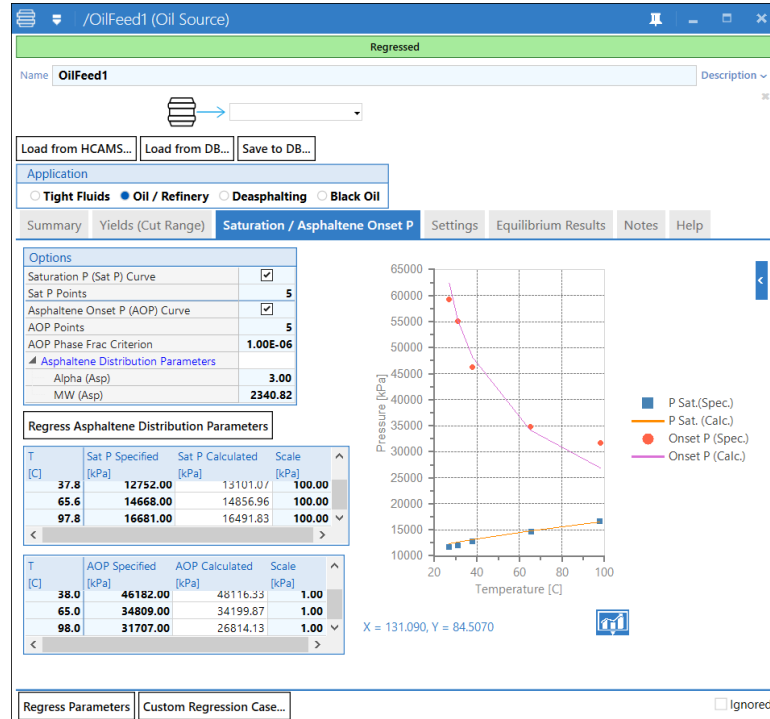


Note how the Yield and Density parameters had been adjusted to match the Saturation Pressure and Stock Tank Oil properties. Now click on the *Asphaltene Onset P (AOP) Curve* box from the Saturation / Asphaltene Onset P tab to add the asphaltene onset pressure data from Gonzalez et al. [2].



Observe that there is an extra parameter called *AOP Phase Frac Criterion*, this is the mole phase fraction value at which one can consider the appearance of an asphaltene phase. The default value is 1E-06 but can be customized or used as tuning parameter if necessary.

Now click on the *Regress Asphaltene Distribution Parameters* button, this will adjust the average molecular weight of asphaltenes, MW (Asp) parameter, to match the asphaltene onset pressure. Once the regression is done observe the new results.



Now the Oil Source has found the best fluid compositions that can match Stock Tank, Saturation and Asphaltene Onset Pressure data.

We can do now more studies using other tools from the Oil Source, like plotting saturation and asphaltene onset pressure lines with no more tuning required. To do, so go back to the Summary tab and click the *Asphaltene Calculations* box from the *Options* frame.

The screenshot shows the 'OilFeed1' configuration window. The 'Saturation / Asphaltene Onset P' tab is active. In the 'Bulk Experimental Variables' section, the 'Asphaltene Calculations' checkbox is checked. The 'Reference Conditions' section shows 'Liq. Ref. P [kPa]' set to 101.33. The 'Material' section shows various flow and property values.

Names	Active	Specified	Calculated	Scale
Stock Tank Oil Density [kg/m ³]	<input checked="" type="checkbox"/>	919.0000	905.3310	1.0000
Stock Tank Oil MW	<input type="checkbox"/>		174.81	1.00
Gas to Oil Ratio (GOR) [Sm ³ /m ³]	<input checked="" type="checkbox"/>	100.63	98.82	1.00

SARA Distrib. (Stock Tank Oil)	
Saturates (mass) [%]	39.36
Aromatics (mass) [%]	36.04
Resins (mass) [%]	9.04
Asphaltenes (mass) [%]	15.56

PortName	Out
Is Recycle Port	<input type="checkbox"/>
Connected Stream/Unit Op	
VapFrac	0.5522
T [C]	60.0
P [kPa]	101.33
Mole Flow [kmol/h]	1.00
Mass Flow [kg/h]	108.35
Volume Flow [m ³ /h]	15.063
Std Liq Volume Flow [m ³ /h]	0.137
Std Gas Volume Flow [Sm ³ /d]	5.6857E+2

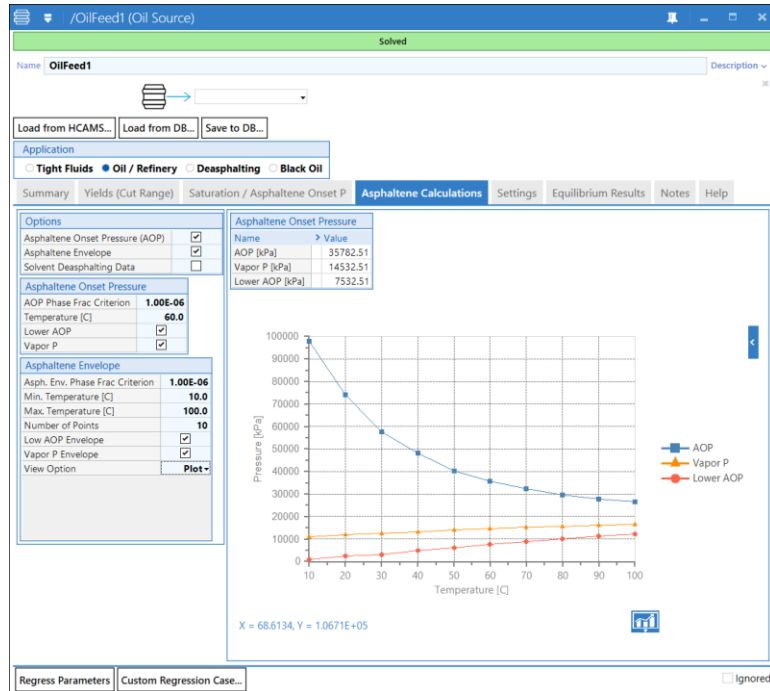
This enables a new tab called Asphaltene Calculations. Here single point or envelope onset pressure calculations can be done. The calculation results can be reported in Table or Plot formats:

The screenshot shows the 'OilFeed1' configuration window with the 'Asphaltene Calculations' tab active. The 'Asphaltene Onset Pressure' and 'Asphaltene Envelope' sections are visible. The 'Asphaltene Envelope' section shows a table of results for different temperatures.

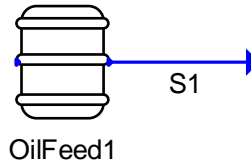
Asphaltene Onset Pressure				
Name	Value			
AOP [kPa]	35782.51			
Vapor P [kPa]	14532.51			
Lower AOP [kPa]	7532.51			

Asphaltene Envelope				
Temperature [C]	AOP [kPa]	Vapor P [kPa]	Lower AOP [kPa]	
10.0	97864.31	10994.11	1040.96	
20.0	74160.01	11793.59	2485.00	
30.0	57546.99	12546.99	3171.99	
40.0	48254.06	13254.06	4754.06	
50.0	40165.48	13915.48	6165.48	
60.0	35782.51	14532.51	7532.51	
70.0	32294.24	15106.74	8919.24	
80.0	29702.41	15639.91	10108.66	
90.0	27852.50	16133.75	11149.37	
100.0	26582.61	16589.93	12054.05	

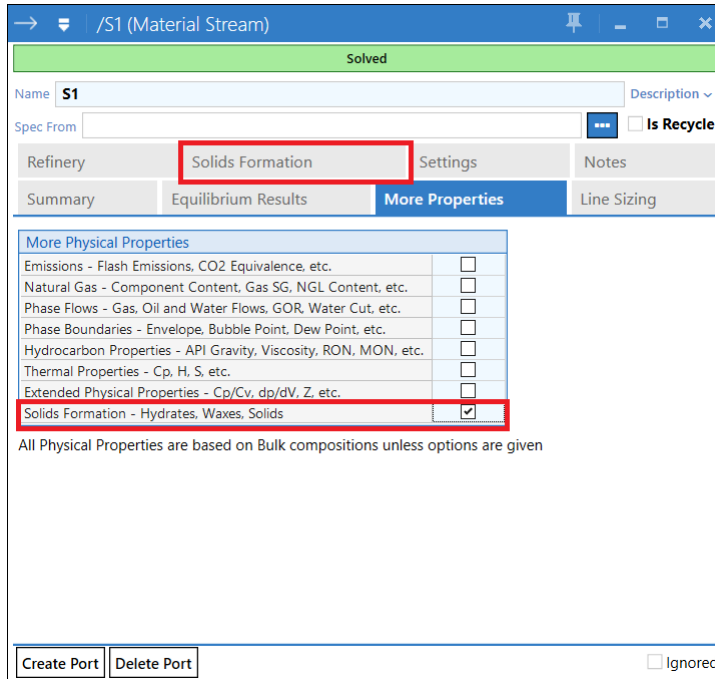
The Plot option shows the phase boundary lines between asphaltene, vapor and liquid phases; this plot can help user to identify the conditions for region where asphaltene precipitation may or may not happen.



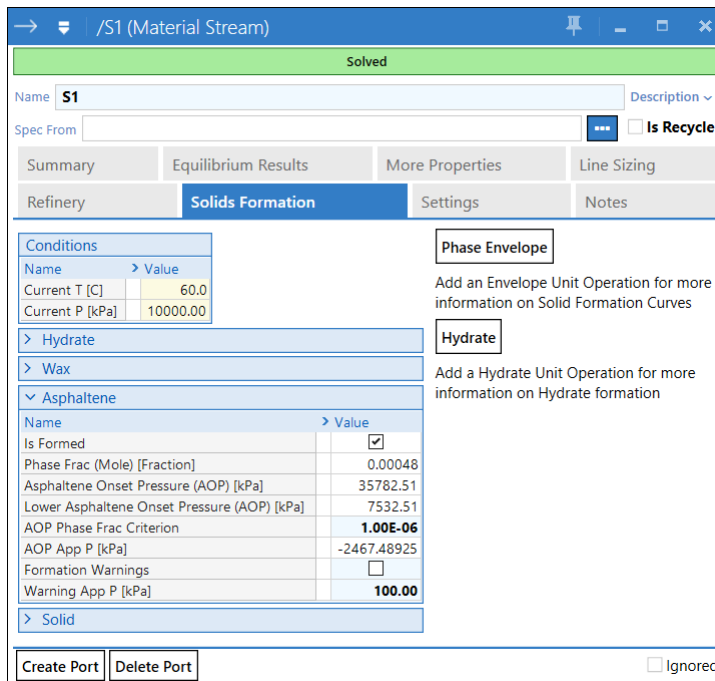
A Material Stream that contains asphaltene-like components can monitor their formation based on the temperature and pressure condition of the stream. To see how this works connect a Material Stream to the characterized Oil Source.



In the Material Stream, go to the More Properties tab and check the *Solids Formation* box, this will open a new tab called **Solids Formation**.



In the Solids Formation Box, open the Asphaltene node to observe the different calculations for asphaltenes.



The calculations include a box to know if the Asphaltenes are formed, the asphaltene mole phase fraction, the Asphaltene Onset Pressure and Approach Pressure, and a box to activate Formation Warnings. The last box is used to set up Material Stream asphaltene formation alarms; if asphaltenes are formed, the status bar of the Material Stream will turn red and show a message about the possible formation. Activate the Formation Warnings box and change the Oil Source Material Port Pressure to 10 MPa, now observe the message in the Material Stream status bar:

Asphaltene forms at these Stream conditions (Approach P [kPa] = -2.47e+03)

Name: S1

Spec From: [] Is Recycle: []

Summary | Equilibrium Results | More Properties | Line Sizing

Refinery | **Solids Formation** | Settings | Notes

Conditions	
Name	Value
Current T [C]	60.0
Current P [kPa]	10000.00

> Hydrate

> Wax

> Asphaltene

Name	Value
Is Formed	<input checked="" type="checkbox"/>
Phase Frac (Mole) [Fraction]	0.00048
Asphaltene Onset Pressure (AOP) [kPa]	35782.51
Lower Asphaltene Onset Pressure (AOP) [kPa]	7532.51
AOP Phase Frac Criterion	1.00E-06
AOP App P [kPa]	-2467.48925
Formation Warnings	<input checked="" type="checkbox"/>
Warning App P [kPa]	100.00

> Solid

Create Port | Delete Port | Ignored

In a flowsheet environment, these alarms can be set up in any Material Stream providing a monitoring asphaltene formation system into your Symmetry process platform flowsheet.

References

- [1] Loria, H. "PIONA Characterization in VMGSim 8.0" VMG's Technical Newsletter, December 2013.
- [2] Gonzalez, D. L.; Mahmoodaghdam, E.; Lim, F.; Joshi, N. *Effects of Gas Additions to Deepwater Gulf of Mexico Reservoir Oil: Experimental Investigation of Asphaltene Precipitation and Deposition*. SPE 159098

To learn more about the Symmetry Process Software Platform please contact your local Schlumberger office.

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