Prediction of Flocculation and Inception of Coking in Refinery Crude Mixtures

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BACKGROUND INFORMATION

The newly updated Automated Flocculation Titrimeter (AFT) automates the collection of Heithaus values and predicts flocculation for various crudes. It also allows users to easily and reliably predict which heavy oils and petroleum residua (including asphalts) can be mixed without causing phase separation.

Typically, refiners all around the world have stopped processing crudes too soon because they couldn't predict precisely when coking would occur. They've stopped well short of coke formation to avoid fouling in heavy oil processing equipment, tanks, and transfer lines but have reduced the distillate yield. That is now history due to the development of the advanced AFT. This advanced laboratory tool is also capable of reverse titration and can be used for flocculation kinetic studies.

This expanded AFT methodology, now allows any refinery using this tool to recover additional distillate without fear of fouling. One can predict the refinery conditions for coking and stop processing before fouling occurs but not sooner than necessary by using the Coking Indexes pioneered by Western Research Institute. The AFT lets the user quickly and easily collect the data needed for analysis.

The theory behind this innovative technique is discussed in this poster as well. Petroleum residua consists of ordered structures of associated polar asphaltene complexes that are dispersed in a lower polarity solvent phase by intermediate polarity material commonly referred to as resins. When the residuum is heated to temperatures above 340 degrees Celsius, this suspended structure is systematically and irreversibly destroyed during pyrolysis. A common problem in the refining industry is to ascertain how close a pyrolysis system is to forming coke on the coke induction period timeline. A certain amount of pyrolysis typically occurs and can be tolerated in a distillation unit, since there is an induction period prior to the appearance of coke.

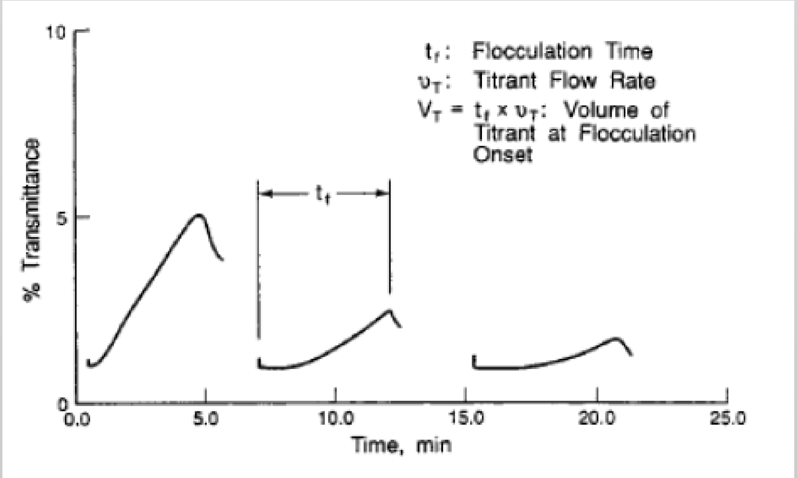
The automated flocculation titrimeter has been developed to perform ASTM D6703, the official test method for automated Heithaus titrimetry. This helps to measure the state of the dispersed particle system and calculates predictive parameters for heavy oils.

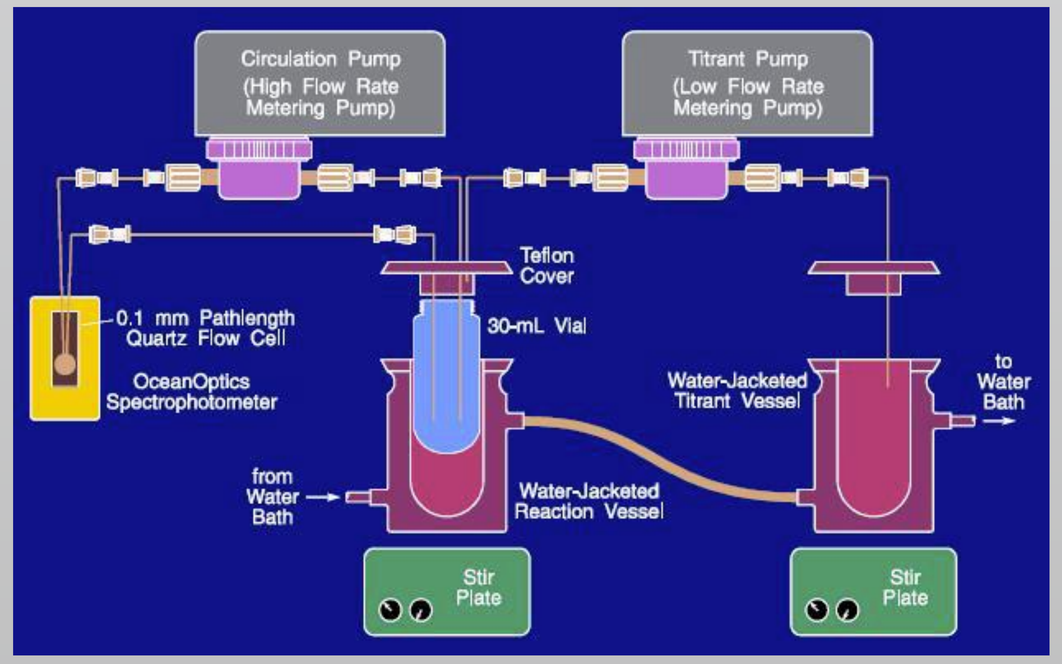
The advanced AFT can now be used to provide valuable information about the internal stability of a heavy oil, the proximity of a pyrolyzed oil to coke formation, and to design blending protocols for oils mixtures related to prevent asphaltene precipitation, as well as study flocculation kinetics. It is an extremely versatile tool for the petroleum industry in both upstream and downstream operations.

INSTRUMENTATION AND TEST PROCEDURES

The Automated Flocculation Titrimeter (AFT) pictured to the left was developed to perform ASTM D6703 which measures the state of the dispersed particle system and calculates predictive parameters for heavy oils.

- Three portions of oil samples (0.4 g to 0.8 g) are weighed and dissolved in 2 ml of toluene solvent to provide different concentrations.
- Iso-octane (2, 2, 4-Trimethyl pentane) or some other titrant at a low constant delivery rate (0.1 to 0.5 ml/min) is used to titrate the toluene solutions in sealed vials.
- Both the titrant and sample vials sit inside water-jacketed beakers that connect the external heating/cooling bath to control the temperature between 20°C and 100°C.
- Mini magnetic stirrers inside these vials make sure the solutions are homogeneous. The uniform solutions are circulating through a flow quartz cell that connects to spectrometer by two optical sensors.
- The output signal from the spectrometer is recorded as percentage of light and graphed along the time by special designed AFT software.
- The change in percent transmittance (%T) of detected radiation measured at 740 nm passing through the quartz cell is plotted versus time, t





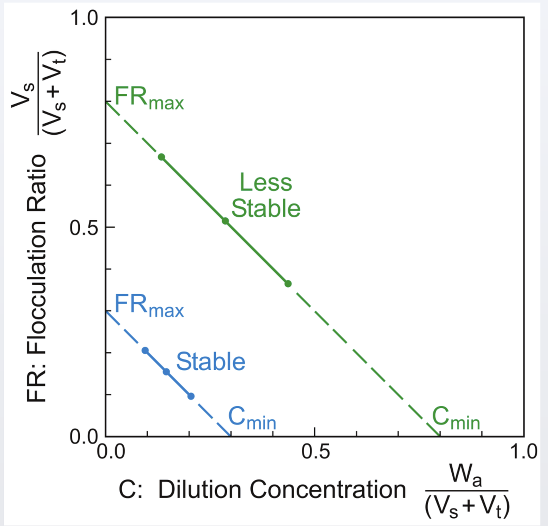
The AFT performs the titration in a closed-looped glass and Teflon system to prevent evaporative solvent losses and to eliminate fouling of metal surfaces, the schematic is shown to the left

RESEARCH AND RESULTS

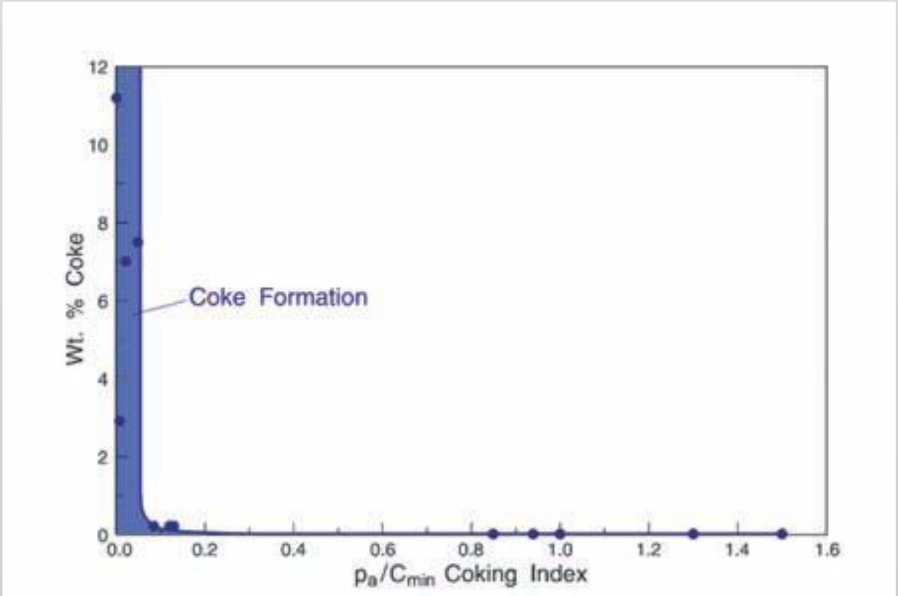
Once titration is completed, the data is exported to excel and a plot of the parameters is generated. A plot of FR vs. C is made. FR is the flocculation ratio, obtained by dividing the volume of toluene by the total volume of solvent and titrant used up to the point of flocculation. C is the dilution concentration obtained by dividing the weight of the crude oil by the volume of solvent and titrant used up to the point of flocculation.

From the FR vs. C plot the X and Y intercepts are measured, where FR_{max} is the Y-intercept and C_{min} is the X-intercept. The latter is the ratio of the weight of oil to volume of titrant at the onset of flocculation with zero toluene present. FR_{max} is the volume fraction of toluene in the toluene/titrant mix at the onset of flocculation at zero oil concentration.

Several useful parameters are derived from the data obtained with the AFT. The stability value, P, is automatically calculated as $1 + (1/C_{min})$. This value is an indicator of the internal stability of an asphalt or heavy oil residuum.



Flocculation Parameters										
v_T (ml/min)	T_p (s)	Wt (g)	V_s (ml)	V_t (ml)	C (g/ml)	FR	δ_{Oil}	V_s'	V_t'	S_{BN}
0.300	468.41	0.40000	3.00000	2.34205	0.0749	0.5616	8.87	7.50	5.86	102.90
0.300	523.343	0.80000	3.00000	2.61672	0.1424	0.5341	8.85	3.75	3.27	101.55
0.300	465.18	0.40300	3.00000	2.32590	0.0757	0.5633	8.83	7.44	5.77	100.19
Calculated Heithaus Parameters		m =	-0.4213		pa =	0.459		m(V') =	0.6832	
		y0 =	0.5941		po =	1.0155		y0(V') =	0.7086	
		C_{min} =	1.4102		P =	1.7091		FR 5/1 =	0.5099	
		dF =	8.29021		IN =	59.414		S_{BN} =	101.54	



The AFT Parameter pa is related to the polarity of asphaltenes, equal to $(1-FR_{max})$. A typical pa for an unpyrolyzed residuum is near 0.6. As a residuum is pyrolyzed and asphaltenes become more polar, the pa value subsequently decreases. Additionally, as a residuum is pyrolyzed, the C_{min} value increases.

The C_{min} and pa values are used as a basis to determine the WRI Coking Index (the ratio of pa/C_{min}). Values typically around 1 or higher for highly stable residua (Schabron et. al. 2001). As a residuum is pyrolyzed, the pa/C_{min} value decreases to a threshold value of about 0.2, below which coke has formed.

CONCLUSIONS

The automated flocculation titrimeter has been developed to perform ASTM D6703, the official test method for automated Heithaus titrimetry. This helps to measure the state of the dispersed particle system described above and calculates predictive parameters for heavy oils. With the advanced development, the AFT can now also be used to provide valuable information about the internal stability of a heavy oil, the proximity of a pyrolyzed oil to coke formation, and to design blending protocols to prevent asphaltene precipitation for oils mixtures, as well as study flocculation kinetics. It is an extremely versatile tool for the petroleum industry in both upstream and downstream operations.

ACKNOWLEDGEMENTS

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