Reduction of Fouling Due to Heat-Induced Deposition and Coking Using Automated Flocculation Titrimetry

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Background

In the refining industry, heat induced deposition and undesirable coke formation occurs from thermal processes. At temperatures above 340 ˚C, pyrolysis takes place which leads to the destruction of the solvation cell and intermediate polarity material. Heat-induced deposition and coking ensues resulting in fouling. The typical solution is to cease the distillation early and use lower heating profiles. The premature termination of the process results in economic lost due to downtime. The introduction of the Automated Flocculation Titrimeter (AFT) allows the presence of coke formation to be predictable. The data collected works with the Coking Index developed by Western Research Institute. The WRI Coking Index is an indicator for proximity to coke formation. The AFT instrument is valuable for minimizing fouling produced by heat induced deposition and coke formation.

Instrumentation

The Automated Flocculation Titrimeter (AFT) performs ASTM D 6703, an established technique for automated Heithaus titrimetry. The process starts with at least two samples of oils being weighed and dissolved in toluene. A titrant such as isooctane or heptane is utilized to titrate the solutions. The solutions are kept uniform and are connected to a spectrometer with the use of optical sensors. The output from the instrument is the percentage of light transmitted and is graphed with respect to the volume. The decrease in transmittance at 740 nanometers is measured as flocculation.

Figure 1 (Above)
Automated Flocculation Titrimeter

Data

Once titration is complete, a plot is made of the flocculation ratio (FR) versus the dilution concentration (C). The FR is the volume of the toluene divided by the volume of the titrant-toluene solution at flocculation. The C is weight of the oil divided by the volume of the titrant-toluene solution at flocculation. Figure 3 portrays pyrolyzed and unpyrolyzed residua. The y-intercept is represented by FR_{max} which is a fraction between 0 and 1. The x-intercept is labeled C_{min} and is the ratio of oil weight to titrant volume when no toluene is present.

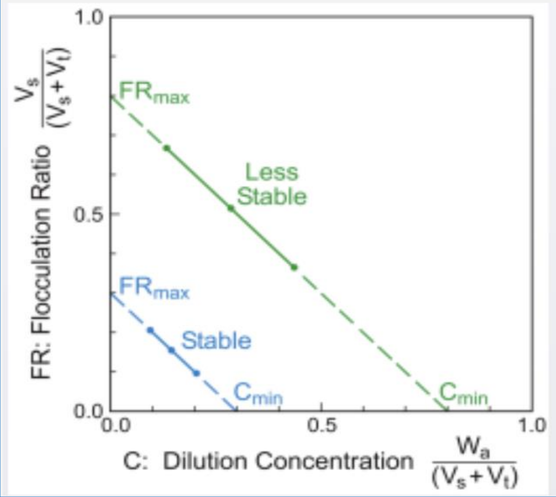

Figure 3 (Left) Flocculation Ratio vs. Dilution Concentration

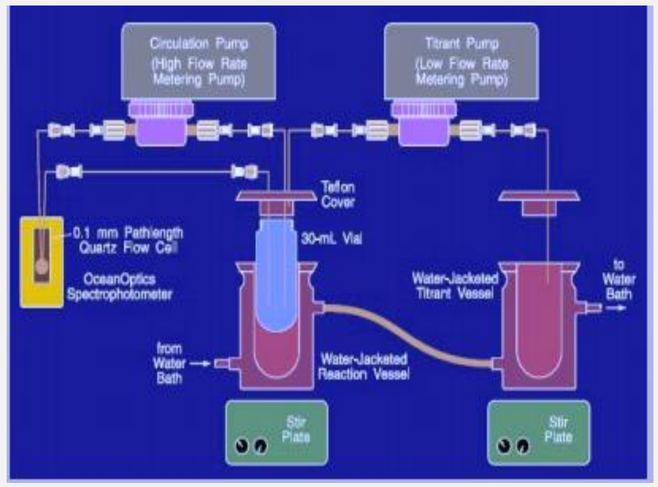

Figure 2 (Above) The closed system is made of Teflon to prevent any solvent loss and fouling of the instrument

Results

The AFT data provided can predict the stability of the asphalt or oil residua. The stability value, P is formulated as $1 + (1/C_{min})$. The value of P ranges between 2 and 10 with a greater number representing more stability. The calculation of the heptane asphaltene's weight percentage provides the parameter known as free solvent volume. The free solvent volume is a value between 0 and 1 which labels the ordering of the residuum. This parameter aids in predicting the conditions where heat induced deposition occurs. Stability collaborates with the free solvent volume in minimizing heat induced deposition. The free solvent volume indicates the measure to which the solvent is bound by the solvated core. A higher free solvent volume is considered more stable and is more desired. A higher value means the solvent is more bound making it less vulnerable to heat. This lessens the risk of heat induced deposition and coke formation. Additionally, higher temperatures increase the risk of deposition because the solvation shell is removed, and the polar cores are exposed to the metal surface. A low temperature setting in tandem with a high free solvent volume minimizes heat induced deposition.

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	

Table 1 (Left) Typical set of test results

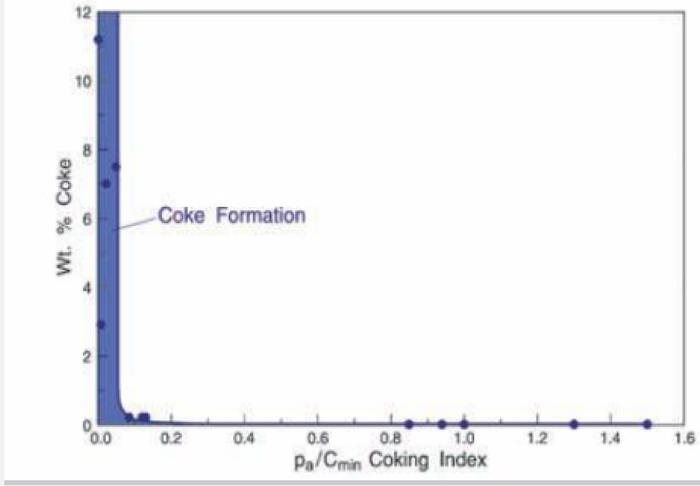

Figure 4 Wt.% Coke vs Coking index. Coking occurs when the Coking Index value is less than 0.2

The polarity of the asphaltenes is represented by the value pa. It is calculated as $(1 - FR_{max})$ and assists in measuring the proximity to coke formation. The WRI coking index uses the ratio pa/C_{min} to predict coke formation. A stable value for the WRI coking index is 1 and coke formation happens at about 0.2. The pa value decreases and the C_{min} value increases when the residuum is pyrolyzed. This decreases the overall value of the ratio resulting in its value reaching less than 0.2.. Fouling can be minimized by preventing pyrolysis. In return, the residua are more stable, and the free solvent volume is higher. This prevents heat induced deposition and coke formation.

Reference

Dr. John. F. Schabron, Principal Scientist & Dr. Raj Shah, Director, "Automated Flocculation Titrimetry to Optimize Distillate Yield and Minimize Fouling", 2006, Western Research Institute