

Heavy Oil and Bitumen Analytical Methods: Understanding Their Capabilities and Limitations

Project Review & Update
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CCQTA

The Canadian Crude Quality Technical Association

Background

- Many petroleum methods were developed for light crudes and are not easily applied to heavy oils and bitumens
- Over the last 30 years experienced users have developed special handling techniques and modification for application to bitumen
- A considerable data base related to heavy oil methods has been collected in terms of reviews and round robins

Project Goal

- To document the capabilities and limitations of heavy oil and bitumen methods to allow users to make informed decisions on method selection
- Not to provide detailed method descriptions

Targeted Methods

- Sample Preparation
- Chlorides
- Asphaltenes
- Distillation
- TAN
- Sulfur
- Density
- BS&W
- Viscosity

Sample Preparation

- One of the most overlooked challenges in analytical chemistry
- Cleaning method of choice depends on the analysis method and nature of the sample
- Bitumens and emulsions are particularly difficult

Sample Preparation

- Most common methods are centrifugation and filtration; however, they often are not applicable to heavy oils
- Solvent extraction or distillation are more useful for heavy oil and bitumen
- All data should include a statement on the sample preparation used

Asphaltenes

- Bitumens and heavy oils contain high quantities of asphaltenes
- Asphaltenes may precipitate during recovery operations due to pressure drop, acids, CO₂ and condensate addition, and incompatibility
- The asphaltene fraction is a precursor of coke formation, and thus a measure of upgrader feedstock quality

Asphaltenes

Many ASTM, UOP and IP methods are available; however, the following guidelines apply:

- N-pentane or n-heptane precipitants
- 40 mL precipitant per g sample
- 2 h contact time in the dark
- Samples dispersed in toluene (1:1) prior to n-pentane addition; samples refluxed in n-heptane

Total Acid Number

- TAN was originally developed to indicate the quality of petroleum products and used lubricating oils
- TAN is used as a measure of naphthenic acid corrosion potential of crudes, but presents challenges when applied to bitumen

Total Acid Number

- ASTM D664 was modified by CCQTA to handle heavy oils using pre-dilution with toluene
- UOP 565, Procedures B and C, would require extensive modifications for application to heavy oils
- ASTM D974, colorimetric method, is not applicable to heavy oil

Density

- Density (or API gravity) is a major criterion in setting crude prices
- Conversion tables (ASTM D1250) are frequently used for converting densities to the 15°C reference temperature
- Bitumens typically have densities $>1000 \text{ kg/m}^3$ ($<10^\circ \text{API}$)

Density

- ASTM D4052, digital density meter, is fast and reliable for bitumen
- ASTM D70, pycnometer, is reliable and precise for bitumen, but is time-consuming
- ASTM D71, displacement method, is useful for small samples, but both it and the previous method may have surface tension issues
- ASTM D1298, hydrometer, may be applied to bitumen, but is tedious and requires large sample

Viscosity

- Viscosity of crude impacts viability of production techniques
- Pipelining requires crude to meet viscosity criteria; dilution is required for bitumens
- It is generally assumed that bitumen is Newtonian, but some instances of non-Newtonian behavior have been observed

Viscosity

- ASTM D445, kinematic capillary viscometer, may be used for bitumen. For $>10,000$ cSt and for samples with water which may be non-Newtonian, cone-and-plate is more appropriate
- ASTM D3205, dynamic cone-and-plate viscometer, applicable for 10^3 to 10^{10} P and non-Newtonian behavior; commonly used for bitumen even though it was withdrawn in 2000

Chlorides

- Inorganic chlorides (water soluble) affect primary distillation towers; salt levels are used to optimize desalting units
- Organic chlorides (hydrocarbon soluble) historically linked to corrosion in hydrotreating units
- Recent evidence to suggest that organic chlorides play a role in crude unit corrosion

Chlorides

- ASTM D6470, salt in crude, by dissolution in xylene and aqueous extraction; testing for halides by potentiometry, is applicable to most heavy petroleum products
- ASTM D4929, determines organic chloride in the naphtha fraction (sodium biphenyl reduction or oxidative combustion/microcoulometry); most heavy oils contain very little naphtha

Distillation

- Most basic and important separation process in refineries and also in the lab
- Distillation curves provide an important set of data in its own right, but distillation cuts also simplify compositional analysis

Distillation

Vacuum Distillations (*actual cuts obtained for further analysis*)

- ASTM D2892 and D5236 are most commonly used for bitumens (up to 538°C and 15 theoretical plates)
- Spinning band (up to 450°C and 50 plates)
- Short path (up to 700°)

Distillation

Simulated Distillations by GC (no cuts) to produce curves)

- ASTM D7169, most applicable to bitumen, provides sample recovery to 720°C
- ASTM D6352, for cuts with FBP < 720°C
- ASTM D5307, for bitumens, provides sample recovery to 538°C
- ASTM D2887, applicable to cuts with FBP < 538°C

Distillation

Things to Watch out for with Vacuum Distillations of Bitumen

- Water – causes bumping
- Flooding the column – must watch
- Cracking – thermal degradation may occur between 250-350°C - fogging, drop in vapor temperature

Sulfur

- Bitumens and heavy oils can contain up to 5% S, much higher than light to medium crudes
- Sulfide, mercaptan, thiophenes are common, and speciation can be important to refiners with respect to potential for catalyst contamination and corrosion
- Removal of S is key to meet new ultra low specs of products

Sulfur

- ASTM D2622 and D4294, X-ray methods, are applicable to heavy oils, but are matrix dependent; matrix matching calibration standards to samples
- ASTM D1552, oxidative microcoulometry (LECO method), also applicable to heavy oils
- Generally LECO and X-ray data are equivalent, but certified standards are required to reduce inter-lab biases

BS&W

- Measure of solids and free water in crude or emulsions
- Used as estimate of fluids composition in SAGD
- Spec test for crudes and dilbit for pipelines
- In determination of net oil volumes in sales, taxation and custody transfers

BS&W

- ASTM D4007, centrifuge method is applicable to heavy oils, but emulsions may be problematic; accepted method in custody transfers
- For more accurate results, D4006 (distillation) or Syncrude modified Dean-Stark should be used

Future Areas of Investigation

- Carbon, hydrogen, nitrogen and oxygen
- Molecular weight
- Carbon residue
- Ash
- Nickel and vanadium
- Flash point
- Pour point