Laboratory standards on the characterization of heavy crude and bitumens : Part IV. Third round of tests on Cerro Negro crude

Majid, A.; Boyko, V.; Clancy, V.; Lamb, K.; Web, A.; Toll, F.

Publisher's version / Version de l'éditeur:
https://doi.org/10.4224/21270105
IEC Report, 1992-12-01

National Research Council Canada
Conseil national de recherches Canada

Institute for Environmental Chemistry
Institut de chimie de l'environnement

Process Technology
Technologie des procédés

NRC-CNRC

APPROVALS

APPROBATIONS

DECEMBER1992
EC-1260-92S

LABORATORY STANDARDS ON THE CHARACTERIZATION OF HEAVY CRUDE AND BITUMENS. PART IV. THIRD ROUND OF TESTS ON CERRO NEGRO CRUDE

A. MAJID, V. BOYKO, V. CLANCY, K. LAMB, A. WEB AND F. TOLL

Submitted By
Soumis par

Project Leader Chef de projet

Approved By
Approuvé par

Program Head Dirigeant de programme

Approved By
Approuvé par

Director General Directeur général

Ottawa, Canada
K1A 0R6

Docufax: (613) 941-2529

Canada

INTRODUCTION

The work described in this report lists the results of a round robin study on a heavy crude sample from the Orinco Tar Belt in Eastern Venezuela. The UNITAR Centre for Heavy Crude and Tar Sands coordinates these round robins for the classification and characterization of heavy crudes. These round robins were initiated by ACOSA (Alberta Committee on Oil Sands Analysis) in 1982. As part of our mandate to help other organizations and industries and as a gesture of international cooperation we have been participating in these round robin studies ever since. The objective of these round robin studies was revised in the form of a protocol agreed upon by the representatives of participating laboratories at a meeting in February 1992 in New York. This protocol is the first step towards standardization and will be continuously enhanced as the effort progresses. The main elements of this objectives are as follows:

- Further standardize procedures for the evaluation of whole heavy crude samples,
- Continue to build the data bank on the characterization of heavy crudes and bitumens on an international basis,

- **Provide information to participating laboratories for automatic evaluation of their operations, and**
- **The methods and procedures for the characterization of heavy crude and bitumen samples will follow as a second phase of this programm.**

A total of 22 laboratories (including NRC) from eight (8) countries are participating in this latest round robin collaborative study.

EXPERIMENTAL

Materials. **A sample of Cerro Negro Crude from the Orinoco Tar Belt in Eastern Venezuela was provided by Intevep, Venezuela. They used the following steps for sample preparation:**

- **Five 200 L barrels were received from the producing fields.**
- **Two barrels were heated to a temperature just below 50°C.**
- **Barrels were mixed on a roller for five hours.**
- **20 L batches were distilled atmospherically in a distillation unit according to ASTM Standard Test Method D- 2892.**

- **The dehydrated portions were collected in 200 L drums and homogenised by mixing on a roller for five hours.**
- **This homogenized dehydrated whole crude sample was canned in one gallon containers for distribution.**
- **Distilled light ends were added back in**

After arriving at NRC, the crude was transferred at room temperature into 1L brown glass containers and homogenized by mixing on a roller for 3 hours before subsampling.

Pentane and Heptane used for asphaltenes determination were 99% pure chromatographic grade from Fisher Scientific. All other chemicals used were of reagent grade.

Density. **Density was determined using ASTM Test Method 1298 employing an hydrometer. Since, the oil was too thick at 25°C and 30°C, the measurement was made at 40°C using API hydrometers, and the density at the desired temperatures calculated using international conversion tables. From the hydrometer value at the observation temperature, the API gravity and the**

density at 15°C can be calculated using international tables. The density at the desired temperature (X°C) was then calculated as follows:

Density at X°C = Factor (from temperature tables) x Density at 15°C

The values thus determined are given in the following table:

	Run # 1	Run # 2
Observed Temperature, °F	104	104
API reading at 106°F	10.1	10.0
API gravity at 60°F (from table)	8.0	7.9
Density at 15°C	1.0137	1.0145
Density at 25°C*	1.0077	1.0085
Density at 30°C**	1.0044	1.0053

* 0.9941 (Factor for 25°C) x density at 15°C
** 0.9909 (Factor for 30°C) x density at 1.0044

Elemental Analysis. C, H and N analyses were carried out using a combustion method with a Perkin Elmer model 240 C, H, N analyzer with acetalnilide as a calibration standard. Sulphur was determined using two different methods: 1). by x-ray fluorescence using a Phillips PW-1040 x-ray fluorescence spectrometer with ferrous ammonium sulphate as the calibration standard, and 2). by a Leco SC32 sulphur analyzer. Oxygen was determined by ignition in nitrogen followed by coulometric titration of the evolved CO_2.

Carbon Residue. Ramsbottom Carbon Residue was determined using ASTM test method D524. The sample had to be warmed to 65°C in order fill the vessel. Sample sizes used for the two determinations were 1.7g and 0.4g respectively.

Kinematic Viscosity. Kinematic Viscosity was determined at 80°C and 100°C using ASTM test method # D445, employing a Cannon-Fenske Viscometer with about 25 mL of the sample. Samples were preheated to 65°C, filtered and mixed before charging the Viscometer.

Pour Point. The Pour Point was determined using ASTM test method # D97.

Ash Content. Oil was accurately weighed in a 500 mL preweighed porcelain crucible. The sample was heated on a low bunsen burner flame to remove the volatiles and finally in a muffle furnace at 730 ± 5°C for 3-5 hours until the weight of the crucible plus ash remained constant. The crucible was cooled in a dessicator and weighed. The weight of the ash was determined from the difference in the initial and final weights of the crucible.

$$\text{Ash wt. \%} = \frac{\text{wt. of Ash}}{\text{wt. of Oil}} \times 100$$

Sample weights ranged from 29g to 260g. Actual sample weights for various determinations are listed below:

Run #	Sample wt.
1	199.01g
2	260.22g
3	125.73g
4	29.4g

Pentane Asphaltenes. **1 - 5g of oil was accurately weighed into a 500 mL Erlenmeyer flask tared to 0.1 mg. These samples were dissolved in a volume of benzene (mL) numerically equal to the sample weights in grams, by shaking on a reciprocating shaker for 2-3 hours. To these solutions 40 mL of chromatographic grade n-pentane was introduced for each mL of benzene previously added. Each flask was stoppered and shaken thoroughly for 5 minutes. The precipitates were allowed to settle in subdued light for 2 hours, with occasional shaking.**

Each suspension was then filtered through a fritted glass crucible of medium porosity, tared to 0.1 mg, into a filtering flask under slight vacuum. The flask was rinsed with n-pentane and the washings transferred to the filtering crucible. Precipitates were washed with n-pentane until the effluent was almost colourless. Original flasks which contained small amounts of precipitate adhering to the walls were dried at 105°C and then weighed to obtain the weight of the asphaltenes adhering to the walls of the flask. The filtering crucibles were dried at 80°C under vacuum. The crucibles were also weighed to obtain the amount of the asphaltenes.

$$\text{n-pentane asphaltenes (wt. \%)} = \frac{\text{wt. of asphaltenes in flask + wt. of asphaltenes in crucible}}{\text{original wt. of oil}} \times 100$$

Sample weights and conditions of precipitation for various runs are listed in the following Table.

	Run #1	Run #2	Run #3	Run #4
Amount of oil, (g)	3.4	3.13	1.61	4.8
Volume of Benzene, (mL)	3.4	3.1	1.6	4.8
Volume of pentane, (mL)	150	125	65	200
Precipitation Temperature, °C	25	25	25	25
Precipitation Time, (hours)	2	2	2	2

Hot Heptane Asphaltenes. 9 - 10g of oil was accurately weighed into a 500 mL round bottom flask tared to 0.1 mg. To this, 40 mL of 99% chromatography grade n-heptane was introduced for each gram of oil and the contents refluxed for one hour. The suspension was allowed to cool to room temperature and then filtered through a soxhlet type cellulose extraction thimble. The residue remaining in the thimble was soxhlet extracted with n-heptane overnight until the solvent was found to be colourless. The residue remaining in the soxhlet thimble was dissolved in benzene and filtered through Whatman filter paper No. 41. The filtrate contained a benzene solution of n-heptane insoluble asphaltenes. The filtrate was transferred to a preweighed 250 mL round bottom glass flask, which was then attached to a Brinkman Rotary Evaporator. The solvent was removed at 70°C under vacuum. The residue in the flask was dried at 70°C, under vacuum to a constant weight. The weight of n-heptane asphaltenes was calculated from the difference in the final (flask plus asphaltenes) weight of the flask and its initial weight (empty flask). The following Table lists the weights of oil and experimental conditions for the various runs.

	Run #1	Run #2	Run #3
Wt. of oil, (g)	9.003	10.195	9.11
Volume of n-heptane, (mL)	400	450	400
Time for reflux, (minutes)	90	120	90
Time for soxhlet extraction, (hours)	15	6	16

Metals Analysis, Method 1. 0.1-0.2g of ash was weighed into a Teflon PFA microwave digestion bomb. 3 mL conc. nitric, 3 mL conc. hydrofluoric and 1 mL perchloric acids were added to the sample. The bomb was closed and processed in a microwave digestion oven designed for laboratory applications so as to maintain an internal pressure of 55-65 psi for 20-25 minutes. After cooling it was evaporated to dryness on a hot plate and then dissolved by warming with a small volume of 1:1 HCl before dilution to the final volume. Ni, Fe and V were analyzed in this solution using Inductively Coupled Plasma - Atomic Emission Spectroscopy (JY 38 ICP - AES), at 1.2 Kw & 16 L/min of Ar at the following λs:

	Ni	Fe	V
λ, (nm)	231.604	259.94	292.402