Geological and physical-chemistry characterization of asphaltite from Colombian Middle Magdalena region

N Bustos\textsuperscript{1}, E Jerez\textsuperscript{2}, L Paez\textsuperscript{1}, and M Roa\textsuperscript{1}
\textsuperscript{1} Universidad de Santander, Bucaramanga, Colombia
\textsuperscript{2} Universidad Industrial de Santander, Bucaramanga, Colombia

E-mail: man.roa@mail.udes.edu.co

Abstract. The massive consumption of fossil hydrocarbons and the absence of new conventional oil reserves, research on unconventional resources is prevalent. The Asphaltite is a substance with high energy value thanks to its composition of high molecular weight hydrocarbons, becomes an energy alternative in the future. In Middle Magdalena region of Colombia, Luna formation emerges with its members Salada, Pujamana, and Galembo of Upper Cretaceous age, which contains a deposit of this type of substances, which can become an economic and energy engine for the region. A representative sample of this asphaltite was taken in the Galembo Member (Top of Luna formation) and a geological description was made about its formation and occurrence in the area. The solubility of asphaltite was evaluated in two characteristic solvents for hydrocarbons, toluene and heptane, the first of aromatic character, with which it was possible to solubilize probably corresponding to the light fractions, while solubilization with heptane generated a precipitate Asphaltene, a nature that was corroborated by tests of visible infrared and ultraviolet spectroscopy, additionally an elementary analysis was performed to determine the concentrations of carbon, hydrogen, sulphur and oxygen. Finally, by means of thermogravimetry and differential scanning calorimetry an analysis was carried out to evaluate its energy potential, according to the results obtained, asphaltite samples are a promising energy resource.

1. Introduction

The terms: bitumen, asphalt, asphaltite, asphaltite, and bitumen are synonyms, and their use depends on the country. They are related to the mixture of highly viscous organic substances, have typical black color, and would present in the liquid, semi-solid, or solid-state, formed by polycyclic aromatic hydrocarbons soluble in carbon bisulfide [1]. Currently, bitumen’s correspond to 25% of the reserves of hydrocarbons worldwide [2]. Since the 70s, they have been used as additives for drilling fluids, well cementing, inks, pigments for paints and road coating, they are now studied as a possible source of oil and gas [2,3]. These types of materials are mainly composed of high molecular weight polyaromatic hydrocarbons, similar in structure to those expected in the molecular families of resins and asphaltenes present in conventional oil.

In Colombia, the “Agencia Nacional de Hidrocarburos (ANH)”, 2010, has reported outcrops with asphalt in the upper Magdalena Valley, Middle Magdalena Valley, and Caguán, Putumayo basins. The study area is a region with high hydrocarbon production, located in the Middle Magdalena region, where the outcrops of Asphaltite are associated with fractures in rocks of Luna formation (Galembo member) of upper cretaceous age [4,5].
In this article, a geological characterization was carried out on asphaltite collected in field. Subsequently, the solubility of asphaltite in the hydrocarbon solvents was evaluated: Toluene and Heptane; and the fractions obtained were characterized by spectroscopic techniques, comparing them with conventional fluid hydrocarbons of different viscosities. Elemental analysis was also performed to determine the concentrations of carbon, hydrogen, sulfur and oxygen. Finally, by means of thermogravimetry and differential scanning calorimetry, an analysis was carried out to evaluate its energy potential.

2. Materials and methods

2.1. Geological characterization
The Luna Formation is made up of three members: Salada, Pujamana and Galembo, of upper cretaceous age and is considered the hydrocarbon-generating rock in Colombia. The top of Luna formation, called Galembo member, which contains the asphaltite analyzed in this article, is recognized in field for the presence of limestone concretions, carbonate enrichment, phosphate levels, fossiliferous and black calcareous shales [5].

The collected samples (Figure 1) correspond to solid, organic, bright black, light weight and conchoidal fracture material called solid asphaltite or Gilsonite, which usually appears as discontinuous layers of 3 cm to 25 cm thick, arranged between the stratification planes or as filler of fractures in limestones and shales, following a preferential direction 355/70 NE. The Galembo member is limited to the East by the trace of the Lebrija fault, whose structural control printed changes in pressure and temperature that favored the formation of Gilsonite from dense and heavy hydrocarbons.

![Figure 1](image.png)

**Figure 1.** Sample of solid asphaltite (Gilsonite) exhibiting black color and conchoidal fracture.

2.2. Solubility test
The solubility of asphaltite was evaluated in two characteristic solvents for hydrocarbons, toluene and heptane, the first aromatic, while the second aliphatic. 10 grams of asphaltite in 30 ml of solvent was taken. Mixtures were monitored at 24 hours and 48 hours. Asphaltene and maltene fractions were obtained from the dissolution in heptane.

2.3. Spectroscopy characterization
The asphaltenes and maltenes from the asphaltite were characterized by infrared (IR) spectroscopy using Bruker Tensor 27 equipment with attenuated total reflection (ATR) cell, and the Shimadzu UV-240 IPC equipment was used to perform the characterization by ultraviolet or visible light (UV-Vis) spectroscopy of the asphaltenes. The fractions obtained in the solubility tests were compared with the respective spectra of the fractions for conventional hydrocarbons of different viscosities.
2.4. **Elemental quantification**
The determination of the concentration of carbon (C), hydrogen (H), nitrogen (N) and sulfur (S) in the asphaltite sample was carried out, by combustion gas analysis using the Vario CUBE equipment.

2.5. **Thermogravimetry and differential scanning calorimetry**
The asphaltite thermogram of 30 °C to 1200 °C was obtained at a heating rate of 10 °C/min, this was done using Netzsch 449 F1 equipment.

3. **Results and discussion**

3.1. **Geological characterization**
The material collected in the field is bright black, conchoidal fracture and resinous appearance corresponds to Gilsonite-type asphaltite, formed from liquid bitumen that flowed through stratigraphic planes and fractures in sedimentary rocks of the Luna formation (Galembo member) and subsequently it was subjected to higher pressure and temperature conditions generated by tectonic stresses associated with activity of the Lebrija fault.

3.2. **Solubility test**
The solubility of asphaltite was evaluated with two organic solvents, toluene and heptane. Toluene is an aromatic molecule, when mixed with asphaltite, it solubilizes a large part of it, the behavior of the mixture was monitored at 24 hours and 48 hours. After 24 hours the entire asphaltite sample was dissolved, this result is indicative that the majority of the asphaltite sample has molecules with aromatic structure. This structure was verified when analyzing the heptane solubility test, in which it was not possible to completely solubilize the sample, on the contrary, a precipitate formed, this behavior is characteristic of hydrocarbons, in this case the precipitate corresponds to the asphaltene molecules, which, having large polyaromatic nucleus, does not readily solubilize in aliphatic solvents such as heptane. According to these results, two fractions, one soluble and the other insoluble, maltenes and asphaltenes, were obtained by the solubility test in heptane.

3.3. **Spectroscopy characterization**
Figure 2 and Figure 3 show the IR spectra for asphaltenes and maltenes, from asphaltite and hydrocarbons of different viscosities, they show the characteristic signals for alkane groups and aromatic groups, it is observed that in all four cases, the spectra are very similar, reason that indicates that, the 4 types of molecules are very similar [6].

![Figure 2](image-url)  
**Figure 2.** IR spectra of asphaltenes from asphaltite and different oils.
Figure 3. IR spectra of maltenes from asphaltite and different oils.

Figure 4 shows the UV-Vis spectra of asphaltenes from asphaltite and crude oils of different viscosities, a characteristic signal for polyaromatic molecules near 400 nm is observed. As in the case of IR spectra, the spectra are very similar, allowing to conclude that the molecules are structurally similar [7].

3.4. Elemental quantification

Table 1 shows the concentration of C, N, H and S for asphaltite collected in the Middle Magdalena region, according to the concentration of the different elements measured, it coincides with a bitumen type material, in which a high organic carbon content, as well as a low concentration of heteroatoms, said composition also coincides with that expected for a hydrocarbon sample [8-11].

| Element | Concentration (%) |
|---------|-------------------|
| C       | 78.980            |
| N       | 0.860             |
| H       | 7.783             |
| S       | 4.576             |
3.5. Thermogravimetry and differential scanning calorimetry

Figure 5 shows the thermogram obtained for the sample, the greatest loss of mass is seen between 200 °C and 600 °C, equivalent to about 70% of the sample, corresponding mainly to the organic compounds, between 600 °C and 1200 °C, the sample is carbonized, and the losses by organic molecules are minimal, derived from very high molecular weight molecules, the sample has a residual about 25% of the original composition, and they are mainly coal and some inorganic minerals present in it. This thermal behavior reflects the energy potential of asphaltite, in which most of its composition is hydrocarbons [9-12].

![Thermograph of asphaltite.](image)

4. Conclusions

According to the geological analysis, the study sample corresponds to Gilsonite-type asphaltite, which was formed from liquid bitumen, which flowed through stratigraphic planes and fractures in sedimentary rocks of La Luna formation, (Galembo member) and later it was subjected to high pressures and temperatures, associated with the Lebrija fault. The material studied has a composition very similar to that expected for a hydrocarbon, as can be seen in the spectroscopic analysis, where the analyzed fractions have spectra equivalent to those of said fractions for oils and is corroborated by the concentration obtained for elements such as C, N, H and S. The energy potential of this material is manifested in thermogravimetric analysis, where a curve was observed, associated with a high content of hydrocarbon molecules.

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