



## The behavior of Irati oil shale before and after the pyrolysis process



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### ABSTRACT

Oil shale is a sedimentary rock that contains organic complexes of kerogen throughout its mineral matrix. Kerogen can be converted into hydrocarbons through various chemical processes, such as pyrolysis, which is used by Petrobras for oil production in Brazil. To process oil shale, the shale is placed into a vertical cylindrical reactor and subjected to a gas stream that induces pyrolysis at a temperature of 500 °C. The purpose of this study was to examine possible inorganic and petrofabric transformations in oil shales as a result of the pyrolysis process. Samples of oil shale and retorted material (residue from pyrolysis) were analyzed to compare possible chemical, mineralogical and petrofabric variation between the two materials. X-ray fluorescence (XRF), X-ray diffraction (XRD), petrographic analysis and X-ray computed microtomography ( $\mu$ CT) were used for this purpose. Additionally, the effects of temperature and heating rate on the thermal degradation of the samples were determined using thermogravimetric analysis combined with differential thermal analysis (TGA/DTA). The samples of retorted material were obtained with a pyrolysis simulator called BSTU. The chemical and mineralogical results for the oil shale and retorted material showed that the pyrolysis process did not cause significant changes in the rock. The chemical analysis showed that the chemical composition was dominated by SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, while the mineralogical analysis detected mainly quartz, feldspar and clay minerals, as well as pyrite. The thermogravimetric curves showed that organic matter and pyrite decomposed between 400 °C and 550 °C. The main changes occurred in the petrofabric, as the pyrolysis process caused intense fracturing parallel to the original bedding structure of the shale. The process was more pronounced in shales with higher levels of organic matter and led to pore expansion and higher pore connectivity, thus allowing the escape of fluids and gases.

### 1. Introduction

Crude oil is one of the main energy sources of the world. The versatility of oil has made its production a vector for globalization, and oil exploration is a high-risk investment. During the 1990s, the search for new sources stabilized due to the high capacity of oil production. Currently, this situation is changing due to growth in demand and the stabilization of more attractive prices for the development of new petroleum resources (FGV, 2012). The use of new technologies has enabled the discovery of new oil and gas sources. One such development is the exploitation of unconventional fossil fuels related to the energetic potential of hydrocarbons.

Of these unconventional fossil fuels, oil shale is the most common in Brazil. Oil shale is a sedimentary rock that contains an organic complex called kerogen within its mineral matrix. Kerogen decomposes under heat to produce oil and gas (Yen and Chilingarian, 1976). Although oil shale can be found around the world, Brazil possesses the

second largest reserve that contains deposits from various geological periods. However, due to factors such as the thickness and average organic matter content of the deposits, only the Permian-age deposits (278 m.y.a.) are exploited.

Extraction from the oil shale reserve by the Oil Shale Industrialization Business Unit (Unidade de Negócio da Industrialização do Xisto – UN-SIX) of Petrobras S/A involves a technology developed and consolidated by Petrobras, called the Petrosix process. This process aims to extract oil, gas and sulfur from oil shale. The extraction is performed through the pyrolysis of the oil shale by heating the shale in a controlled environment. Prior to the extraction process, the oil shale is placed in jaw crushers that reduce it to fragments 6–70 mm in diameter. The fragmented shale is then placed in a vertical cylindrical reactor (retort), where it is heated by high-temperature gas streams that induce the pyrolysis process at approximately 500 °C. The resulting product, a solid residue known as retorted material, represents 80–90% of the weight of the feedstock and is returned to the mine after processing.

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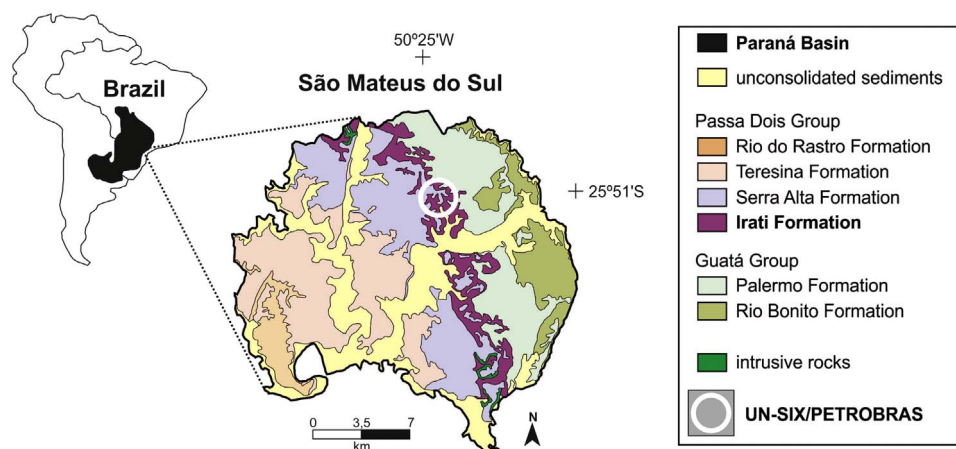


Fig. 1. Geological Map of São Mateus do Sul, East Paraná Basin MINEROPAR (2011).

The mining and industrial area for the oil shale reserve is located in the Oil Shale Industrialization Business Unit of Petrobras S/A in the city of São Mateus do Sul, 140 km from Curitiba, Paraná state, Brazil (Fig. 1). This industrial unit processes ca. 7800 tons of oil shale daily, generating 3800 barrels of oil, 120 tons of fuel gas, 45 tons of liquefied gas and 75 tons of sulfur (Milani et al., 2007).

In terms of geological origin, the oil shale field belongs to the Assistência Member of the Irati Formation in the Paraná Basin (Fig. 1). The São Mateus do Sul region contains two layers of oil shale of economic interest that are separated by an intermediate layer of marls and siltstone. The upper layer has an average oil content of 6.4% and is 6.4 m thick, whereas the lower layer has an average oil content of 9.1% and is 3.2 m thick. Although the lower layer is 3.2 m thick, mining is restricted to 2.4 m of the layer, which has an oil content of approximately 11.5% (Milani et al., 2007).

Studying the effect of the thermal process (pyrolysis) on oil shale generates new knowledge about the efficiency of shale processing and the possibility of designing new technologies for hydrocarbon extraction. It also contributes to a better understanding of the by-products, residues and waste generated by the extraction process. Therefore, the objective of this study was to understand the possible inorganic transformations that take place in oil shale during thermal processing. To this end, samples of oil shale and retorted material (the product of pyrolysis) were analyzed for possible chemical, mineralogical or petrofabric differences.

## 2. Materials and methods

Oil shale samples were collected at the mining location of the UN-SIX of Petrobras S/A, Dois Irmãos mine. Sampling from various lithologies enabled the construction of a lithological profile of the stratigraphy of the two oil shale layers. The profile samples were collected from the mining front at intervals of approximately 30 cm in depth, resulting in an overall lithological profile approximately 18 m deep.

Retorted material was obtained using a bench device that simulated the Petrosix pyrolysis process, called a BSTU (bench-scale testing unit). The device consisted of a vertical bed reactor in which the samples were heated in a controlled atmosphere at a controlled pressure and temperature to induce pyrolysis.

An X-ray fluorescence wavelength dispersive spectrometry (XRF-WDS) technique was used for the chemical characterization of the samples. The mineralogical analysis was performed by X-ray diffraction (XRD) using the pressed powder method and Cu- $\alpha$  radiation with a scan interval of 3–70° 2 $\theta$ . The XRD technique was also used for the identification of clay minerals after decantation, based on Stokes' Law. A transmitted-light petrographic microscope was used to character-

ize the petrographic composition of the different lithologies, including the textural, structural and mineralogical relationships of the rock. In addition, computed X-ray microtomography ( $\mu$ CT) was used in the characterization of microporosity and the identification of minerals.

To determine the effects of temperature and heating rate on the thermal degradation of the samples, a thermogravimetry analyzer (TGA) with differential thermal analysis (DTA) was used at a range of 30–1000 °C and a heating rate of 10 °C/min with an N<sub>2</sub> atmosphere.

## 3. Results and discussion

### 3.1. Characterization of oil shale prior to the pyrolysis process

Prior to the pyrolysis process, the oil shale was a medium/dark grey color with a grain size varying between silt and clay. The silt and clay were deposited in a plane-parallel bedding structure of thin strata less than 1 cm thick, intercalated with organic matter (kerogen). These intercalations were more prevalent in the lower layer than the upper layer. Additionally, plane-parallel oil shale consisting of 1-cm-thick strata of clay minerals and organic matter was observed, intercalated with strata that were richer in organic matter and clay minerals.

The upper layer of the oil shale contained carbonate nodules deposited with their largest surfaces parallel to the bedding and sporadically in cone-in-cone structures. Small (1-mm-thick) calcite laminations aligned with the bedding and bentonite strata (<10 cm thick) were also observed intercalated with the oil shale deposits. The lower layer had 1-mm-thick calcite laminations aligned with the bedding and one bentonite stratum at the interface between the intermediate layer (silt) and the lower layer.

Macroscopic quantification of organic matter showed that the upper layer had a higher organic matter content relative to the lower layer. The organic matter structures appeared under the microscope as circular shapes and in lenses aligned with the rock bedding (Fig. 2). At the bottom of the upper layer, the presence of porous 1-cm nodules and a high bitumen concentration was observed.

The lower layer showed higher average oil content than the upper layer. In addition, average oil content was higher near the top of each layer (Fig. 3). Average oil content varied linearly with the loss on ignition<sup>1</sup> of the oil shale samples (Fig. 4). The plots comparing loss on ignition and average oil content (Fig. 4) show that this linear relationship was related to the escape of organic matter during oil shale processing.

The mineralogy most commonly found in the São Mateus do Sul oil

<sup>1</sup> loss on ignition (L.I.): An analysis in which the sample is heated to 1000°C and total volatile substances are quantified.

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