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Assessment of Uruguayan Oil Shales: physicochemical, thermal and morphological characterization

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ABSTRACT

Oil shales from Mangrullo Formation (Uruguay) was assessed as a potential fuel for energy production. The assessment is based on a comprehensive characterization of the material from a thermal perspective. Co-combustion of this type of fuel with biomass waste can enhance the combustion performance and decrease hazardous gas emissions. The low heating value (3.2 MJ kg^{-1}) of the Uruguayan oil shale indicates that it could be mixed with biomass to obtain better results. Stratified sampling of drill cores was used to obtain a representative sample. The morphological and structural characteristics of the oil shale were studied by X-ray diffraction and scanning electron microscopy. Chemical composition (hydrocarbons and minerals) of oil shales was investigated by X-ray diffraction, X-ray fluorescence, proximate and ultimate analysis and Fourier transform infrared spectroscopy. Rock Eval analysis was performed to measure richness and maturity of the Uruguayan oil shale, the results of the TOC content (8.93%) and the hydrogen index (525 mg HC/ g TOC) indicated that it constitutes an excellent source rock. The kinetic of the combustion and thermal properties of oil shale were studied. The activation energy of the different reaction stages was calculated using the Flynn-Wall-Ozawa model, then we obtained the pre-exponencial factor and the reaction order optimizing the theoretical model using the experimental data. Results indicated that the combustion of the oil shale exhibits multiple reaction stages with activations energies that varies between 152.2 and 316.4 kJ mol^{-1}.

1. Introduction

Oil shales (OS) are fine grain sedimentary rocks that contain organic material of high molecular weight, called kerogen, disseminated in its inorganic matrix [1,2]. These rocks were formed by the accumulation of fine grain sediments and organic matter (such as plankton, algae or rest of plants) in anaerobic conditions, at the bottom of a lake or a sea. During the Early Permian age (Artinskian), a large inland sea developed in the territories that we know today as Uruguay, southern Brazil, Paraguay, South Africa and southern Namibia [3]. The restricted conditions of the sea allowed the accumulation and preservation of high quantities of organic matter, generating the deposition of OS and carbonates.

In Uruguay these lithologies are grouped in Mangrullo Formation [4], called Irati Formation in Brazil [5] and Whithill Formation in South Africa [6]. The Mangrullo Formation is located in northeastern Uruguay, in the departments of Cerro Largo, Rivera and Tacuarembó. Between 1970 and 1990, the National Oil Company of Uruguay (Administración Nacional de Combustibles, Alcohol y Portland-ANCAP) drilled 392 stratigraphic wells in that region to assess the quality of the OS. The studies performed by ANCAP were limited to the identification and quantification of different wells. Samples from the wells were collected for classification and chemical analysis. In some cases, the samples were characterized from a physicochemical point of view. However, these analyses were limited by the technology available at the time. These analyses were made to evaluate the volume of hydrocarbons that can be obtained through pyrolysis of the OS. Through this assessment, it was estimated that approximately 277 million barrels of

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oil (mmbo), could be obtained by pyrolysis [7].

In the last few years, different researches about new applications for OS were reported internationally. Besides the generation of hydrocarbons through pyrolysis, a possible application of OS, used in some countries, is the generation of energy by the direct combustion of the material. Recent works reported that the co-combustion of OS or bituminous coal with biomass have a good performance for energy production with a decreases of the contaminants released to the environment [8–11]. Nowadays, the OS has industrial applications in China and Estonia. In China only for oil production by pyrolysis, but in Estonia also for energy production by combustion using pulverized firing and circulating fluidizing bed [12–18].

Taking into consideration the OS resources that develops in Uruguay and this new and attractive way of energy generation through co-combustion, we propose a comprehensively study of the applications of this resource. To reach the objective of the investigation proposed, it is important to cover the fundamental aspects related with engineering processes and chemistry, focusing on energy production through co-combustion of OS with biomass waste.

In this work, the results of physicochemical, thermal and morphological characterization of the Uruguayan OS are presented. The general objective is evaluate the combustion properties of the Uruguayan OS for the possible future application in the co-combustion with biomass. This is the first time the kinetic of Uruguayan OS combustion is investigated. The results of this work could generate valuable information in other topics such as economic, geology and environmental aspects of the resource, to be consider in a potential exploitation of the resource.

2. Methodology

2.1. Raw material: selection and classification

A set of rock samples (drill cores) corresponding to wells drilled by ANCAP was used (see Fig. 1). The stratigraphy of the wells (Fig. 2) shows two distinctive organic-rich levels (called bituminous seams), separated by a bed of siltstone and limestones. The deeper of these two bituminous seams always shows a higher organic content.

A rigorous analysis of the wells was made to select samples for this work considering the future study of the co-combustion of OS with biomass. The selection of samples was made taking into consideration the depth of the OS levels and physicochemical data (Fischer Assay and Sulfur content) generated by ANCAP in previous studies.

Fig. 1. Map of Uruguay showing the onshore sedimentary basins (in yellow). The black triangle indicates the area explored by ANCAP. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

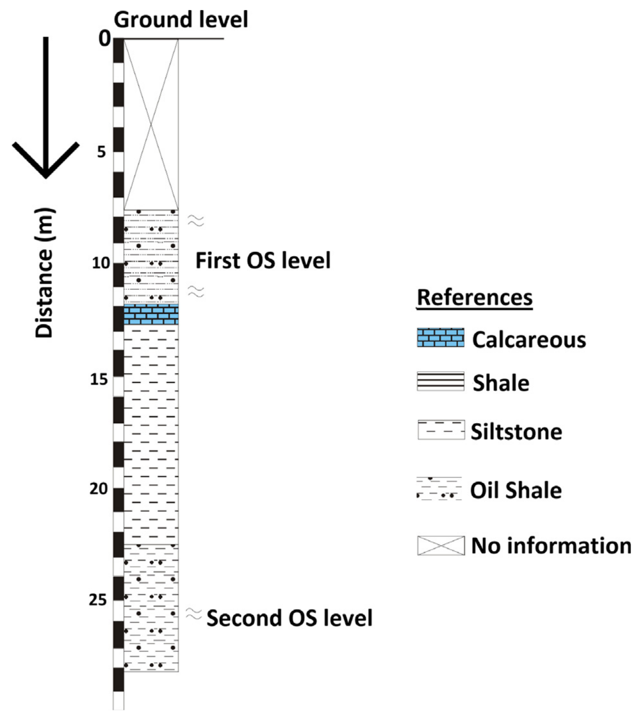

Fig. 2. Stratigraphy of a representative wells.

Sample criteria was based on selecting wells whose second bituminous seam was at a depth up to 35 m and with high oil (>5%) and a low sulfur (<5%). This distance from the ground level takes into consideration a potential mining of the resource. Three wells fulfill that criteria. For this study, the well with the second OS seam closer to the ground level was chosen (approximately 12,5 m, location in Fig. 3).

2.2. Total organic carbon analysis, Rock Eval pyrolysis, Vitrinite Reflectance and Kerogen Microscopy

The total organic carbon (TOC) analysis was performed using 0.15 g of sample. The sample was treated with HCl with the purpose of removing carbonates and then was filtered using fiberglass paper. The

Fig. 3. Map of Uruguay with the location of the selected well indicated in red. Coordinates UTM22S (WGS84) x = 222288, y = 6450242. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)