COGENERATION EMPLOYING THE CAREM MODULAR REACTOR FOR THE PYROLYSIS TREATMENT OF CUTTINGS DERIVED FROM THE OIL AND GAS INDUSTRY IN THE NEUQUÉN BASIN

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Abstract

The Physicochemical and Quality Control Department of the Argentina National Atomic Energy Commission has been actively researching the application of the modular CAREM nuclear reactor for cogeneration, specifically for the treatment of oil-based drill cuttings (OBDC) generated from oil and gas extraction in the Neuquén basin, located in the province of Neuquén, Argentina. These cuttings are classified as hazardous waste under National Law 24051. The objective is to utilize cogeneration to supply heat for the pyrolysis process of the cuttings. This process aims to produce a residue suitable for safe disposal and, concurrently, liquid and gaseous fuels that enhance the intrinsic value of the initial waste.

In the initial phase of the study, samples of OBDC from the Neuquén Basin were employed, collected at depths of 800 m (OBDC-1), 1100 m (OBDC-2), and 1300 m (OBDC-3). The oil content within the cuttings was quantified using Soxhlet extraction (EPA9071B), while the water content was determined through azeotropic distillation using the Dean-Stark method (ASTM-D95). To investigate the thermal decomposition process and the associated energy, a simultaneous thermal analyzer (DTA-TG, STA-409, NETZSCH) was utilized. Furthermore, the mineralogical composition of the remaining residues was scrutinized employing X-ray diffraction.

1.   INTRODUCTION

The CAREM Reactor is a low-power CNPP of 25 MWe, with an integrated self-pressurized primary system. The primary cooling system operates using natural circulation, with multiple passive safety systems. The project is owned by the CNEA (National Atomic Energy Commission) of Argentina and its associated company, INVAP. Since its inception, the reactor has been designed to operate in remote locations [1]. In this sense, considering that Argentina's oil and gas fields are generally located in isolated regions lacking services such as

electrical power, the implementation of a reactor like CAREM can be considered to address power issues and also to provide heat to processes with moderate operating temperatures such as the treatment of oil-based drill cuttings (OBDCs).

The Neuquén Basin, one of the largest hydrocarbon producers in the southern portion of South America, is located east of the Andes Mountain Range in northern Patagonia, Argentina. It covers an area of over 120,000 km^2 [2], currently being the main area for shale oil and gas exploitation in South America, mainly due to the Vaca Muerta Formation, the main source rock.

With the sustained growth in oil and gas production from Vaca Muerta, the generation of drilling cuttings has increased. According to National Law 24051, these cuttings are classified as hazardous waste and are the responsibility of the well owner who generates them. The volume of cuttings generated in drilling a well can vary between 1000 and 5000 m^3 [3]. This range depends, among other variables, primarily on the depth and diameter of the borehole, with a significant portion of the volume generated in the initial stages of the operation, where the diameter of the borehole is generally larger. Regarding their characteristics, the cuttings themselves are inert solids; however, as a result of interaction with drilling fluids, particularly those based on oil (OBDC: oil-based drill cuttings), they reach the surface impregnated with the hydrocarbon constituent of the mud. The tons of OBDC currently generated do not receive on-site treatment and must be transported by trucking companies to treatment plants located far from the wells.

The provided context, along with the current paradigm of comprehensive waste management, which directly involves its minimization at the source, its valorization (recovery, reuse, and recycling), including energy recovery, and finally the implementation of disposal treatments, allows for the formulation of projects related to the cogeneration use of low-power reactors such as CAREM. On one hand, these projects can supply electrical power in oil and gas exploitation areas, and simultaneously, they can treat OBDC with valorization by obtaining value-added products such as liquids and gases enriched in $H_2(g)$, usable as energy vectors or as sources of species of high economic value ($H_2(g)$). Additionally, a solid product suitable for final disposal in dry soil (total petroleum hydrocarbons TPH<10,000 ppm) in accordance with the regulations established in the local province of Neuquén (Resolution (SSMA) 759/09, 2019, Neuquén) can also be obtained.

2. MATERIALS AND METHODS

2.1 Materials: Oil based dril cuttings

The OBDCs belong to the Fortín de Piedra shale reservoir, located in the Vaca Muerta geological formation area, in the province of Neuquén. More specifically, the residues used belong to the Rayoso and Centenario geological formations. In table 1, OBDC-1 corresponds to residues from the Rayoso Formation, extracted at 800 m below the Earth's surface. On the other hand, OBDC-2 and OBDC-3 refer to residues from the Centenario Formation, extracted at 1100 m and 1300 m, respectively.

OBDCs were characterized through proximate and ultimate analysis. Each analysis was performed in triplicate. The water content of OBDC was determined through azeotropic distillation using the Dean-Stark method (ASTM-D95), the ash content was determined by incinerating the sample according to ASTM D2974-20e01 (B) standard, and the volatile matter content was determined by difference. The oil fraction in the samples was determined by Soxhlet extraction using an acetone-hexane mixture (1:1, v/v), following the procedures established in EPA methods 3540 C [4] and 9071b [5].

The determination of carbon, hydrogen, and nitrogen content was performed using a Carlo Erba-Fisons EA 1108 - CHNS-O Automatic Elemental Analyzer, using 2,5-Bis(-tert-butyl-benzoxazol-2-yl)-thiophen, commonly known as BBOT, as the standard, according to ASTM D5373 standard [7]. Then, Oxygen (O) + ASH content was calculated by difference. The summary of results is shown in Table 1.

The ashes were characterized using powder X-ray diffraction (PXRD). The diffractograms of OBDC-1-3 ashes were recorded at room temperature on a BRUKER D8 Advance diffractometer with Bragg-Brentano θ/θ geometry and Cu Kα1 + Kα2 radiation (40 kV, 30 mA) in the 2θ range 5°–90° in steps of 0.02° and with a collection time of 2 s/step. Patterns were analyzed according to standard procedures. The crystalline phases detected in the three samples are very similar (Table 1). These present minimal differences which are mainly feldspars and clays. Figure 1 shows the diffractogram of sample OBDC-1.

TABLE 1. PHISICOCHEMICAL PROPERTIES OF OBDCs

| Properties	OBDC-1	OBDC-2	OBDC-3	Ash	Crystalline Phase/Formula/Ref [7]
Proximate analysis (wt % wet basis)				OBDC-1	Quartz/(SiO_2)/89-8934
moisture	3.31	2.10	2.61		Barite/$BaSO_4$)/80-0512
volatile	15.92	15.53	13.92		Albite/Na($AlSi_3O_8$)/76-1819
ash	78.07	79.12	81.47		Halite/NaCl/89-3615
fixed carbon	2.70	3.25	2.00		Microcline/K($AlSi_3O_8$)/76-1239
Ultimate analysis					Illite/(K, H_3O)$Al_2Si_3AlO_{10}(OH)_2$/26-0911
C	13.38	15.71	14.04	OBDC-2	Quartz/(SiO_2)/89-8934
H	1.26	1.65	1.65		Albite/Na($AlSi_3O_8$)/76-1819
N	-	-	-		Sanidine/(K, Na)($AlSi_3O_8$)/19-1227
S	-	-	-		Illite/(K, H_3O)$Al_2Si_3AlO_{10}(OH)_2$/26-0911
O	7.67	7.03	4.36	OBDC-3	Quartz/(SiO_2)/89-8934
oil content (wt %)	12.54	13.42	12.50		Albite/(Na, Ca)Al(Si, Al)$_3O_8$/41-1480
					Orthoclase/K($AlSi_3O_8$)/75-1190
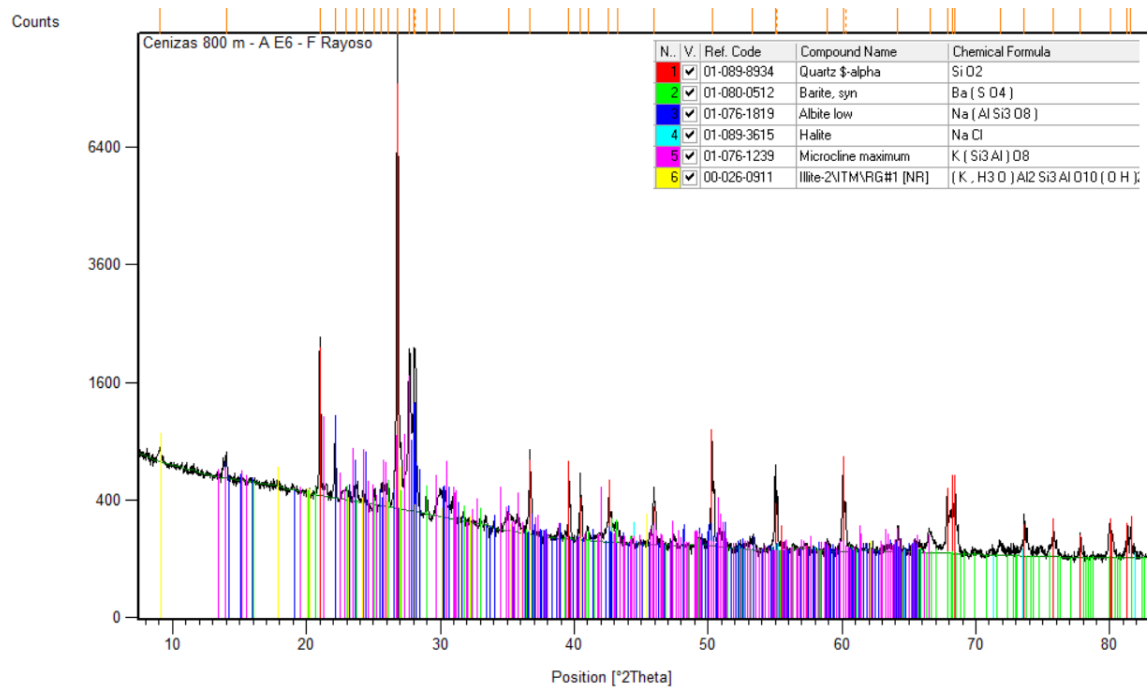
FIG. 1. Powder XRD analysis of OBDC-1 ash, with reference standards of the detected phases.

2.2   TGA and DTA experiments

Simultaneous thermal analysis (DTA/TG) was performed using the NETZSCH STA-409 Simultaneous Thermal Analyzer. The temperature was raised from room temperature to 950 °C, using heating ramps of 10 °C/min, under an inert $N_2(g)$ atmosphere. At this stage of the work, only the results obtained for OBDC-1 are presented.

2.3   Pyrolysis experiments

Pyrolysis experiments were conducted in a stainless steel fixed-bed reactor (Fig. 2). The equipment used includes an electric furnace for heat supply, a pipeline for $N_2(g)$ supply with its respective control, a temperature

controller, and a water-cooled condenser. After loading 10 g of OBDC sample, the reactor was purged for one hour with $N_2(g)$ (1 L/min). For the experiment, the $N_2(g)$ flow rate was reduced to 0.4 L/min, and the system's temperature control was adjusted to raise the temperature at a rate of 15 °C/min and maintain it at a specified final temperature, T_f, of 400 °C, 450 °C, 500 °C, 550 °C and 600 °C for 60 minutes. The condensed water and oil were collected in a 10 ml conical-bottomed test tube to visualize and separate the phases for subsequent weighing. The determination of the yield percentages of each phase was evaluated based on the weights of each component: water, oil, and residual solid, while the yield of non-condensable gases was calculated by difference. The results to be presented correspond to experiments conducted with OBDC-1. Additionally, the total hydrocarbon content of the residual solid residue (char) was evaluated.
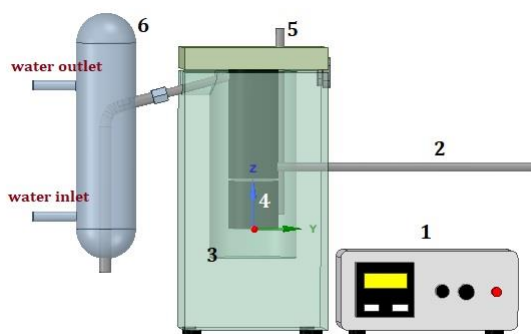

FIG. 2. Experimental set-up used in pyrolysis experiments: 1—PID controller; 2—piline of N_2; 3—electric furnace; 4—stainless steel reactor; 5— K-type thermocouple; 6—water-cooled condenser.

3. RESULTS AND DISCUSSION

3.1 TG/DTG/DTA analysis

The mass loss (TG), mass loss rate (DTG), and DTA curves of OBDC-1 pyrolysis at 15 °C/min are shown in Fig. 3. According to the TG curves, it can be determined that 18 % of the initial mass was lost during the test, which is consistent with the findings reported in Table 1 for the proximate analysis. At approximately one hundred degrees, the DTA curve shows an endothermic peak associated with the release of free water deposited in the pores. The shoulder shape shown in the DTG curve, indicates that it is not only water evaporation. Oven tests for 24 hours at 105 °C showed mass losses higher than the moisture reported in Table 1, indicating the release of light organic compounds as well. The TG curve shows the highest loss, approximately 10 %, between 150 °C and 280°C, with a peak maximum velocity at 242 °C. At this stage, the decomposition and volatilization of aliphatic hydrocarbons, with carbon numbers below C17, and aromatic hydrocarbons with carbon numbers below C12, predominate [8]. The DTG curve exhibits an additional peak at 455°C, indicating a stage of gradual weight loss. According to [8], this phenomenon can be attributed to the volatilization and decomposition (cracking) of heavy organic compounds. The DTA curve displays an endothermic peak at 570°C, with no mass loss as indicated by the TG curve, corresponding to the transformation of alpha quartz to beta quartz [9-10]. The presence of quartz in the sample is evident in the X-ray analysis of the ashes shown in Table 1.
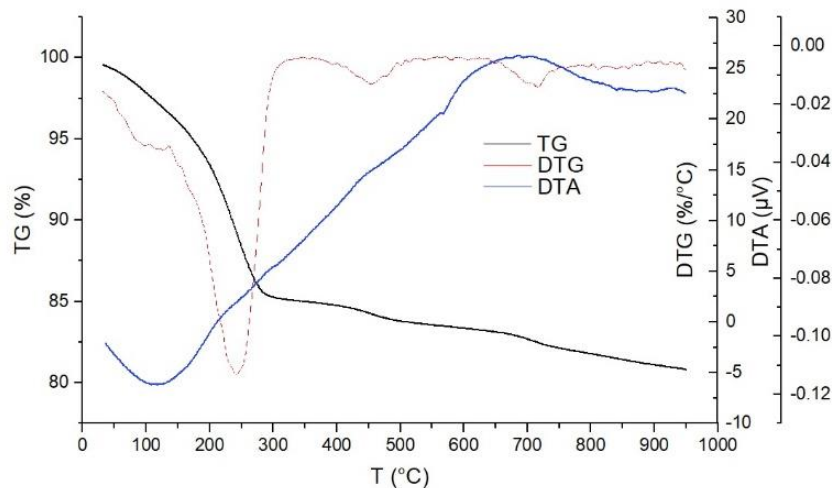
FIG. 3. TG, DTG and DTA curves of OBDC-1 for a heating rate of 10 °C/min.

3.2 Results of the Pyrolysis Experiments

In Fig. 4, the yields of char, oil, gas, and water are shown for a heating rate of 15 °C/min and different final temperatures. It is observed that the production of char is maximum at the lowest temperature studied and then shows oscillations associated with gravimetric determination and the natural non-uniformity of the soil that makes up the cuttings. The higher production of char at low temperatures is associated with the presence of residual heavy hydrocarbons, which is consistent with what was observed in the TGA analysis. The production of water does not show a clear trend. Although the main contribution to the measured water content comes from the free water in the pores, the release of water due to dehydroxylation may also occur in the temperature range of 200-720 °C [10-11] and also during pyrolysis. It is also observed in Fig. 4 that the production of oil shows a maximum at 500 °C.
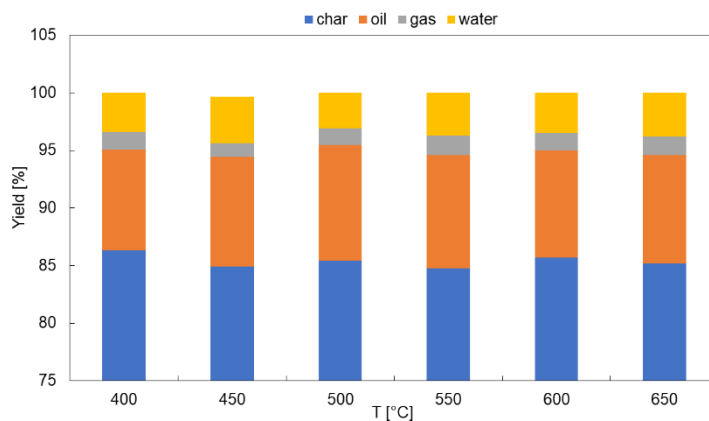

FIG. 4. Product yield from pyrolysis experiments conducted at a heating rate of 15 °C/min, covering a range of final temperatures.

3.3 Determination of oil in char generated in pyrolysis experiments

The oil content in the residual char obtained from the pyrolysis experiments of OBDC-1 was determined through Soxhlet extraction, following EPA methods 3540C and 9071b. The oil content for the residue obtained at 400 °C, 450 °C, and 500 °C was found to be 0.95 %, 0.4 %, and 0.05 %, respectively. These findings are consistent with those observed in the TGA analysis. Consequently, we conclude that the pyrolysis process at 400 °C represents the temperature limit to ensure a residual solid suitable for deposition in dry soil, as per the regulations outlined in Provincial Disposition (SSMA) 759/09 of Neuquén province.

4.   CONCLUSIONS

With the aim of using cogeneration for the treatment of OBDCs using small modular reactors such as CAREM, this work carried out the primary characterization of OBDCs from different formations in the Neuquén Basin. Additionally, thermogravimetric and differential thermal analysis (TG/DTA) experiments and pyrolysis experiences were conducted to measure the yields of char, oil, gas, and water. The obtained char was also analyzed to assess the oil content present. In this regard, it is important to highlight that a low-temperature pyrolysis process (400 °C) can ensure a solid suitable for deposition in dry soil, complying with local regulations. On the other hand, the maximum oil yield is obtained at 500 °C. Increases in temperature above 500 °C result in an increase in the yield of non-condensable gases. The set of results presented allows us to conclude that it is possible to work at relatively low temperatures to generate a clean solid residue and recover oil that could eventually be reused in the drilling process. According to the bibliography, the operating temperatures determined in this work can be achieved through the cogeneration use of the CAREM modular reactor, also solving the need for electrical power supply in the Neuquén Basin fields.

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