EXTRACTION OF MOLYBDENUM FROM SPENT CRACKING CATALYSTS

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ABSTRACT

A catalyst is a substance that changes the rate of a reaction. In the petroleum industry, the catalysts are commonly used for Fluid Catalytic Cracking (FCC) and Hydro Catalytic Cracking (HCC), each of them applied in a specific stage. These catalysts are used to facilitate the molecular chains cracking, which will generate a mixture of hydrocarbons. However, the catalyst gradually loses its activity, either by changing its original molecular structure or by its contamination from other petroleum molecules. The application of ionizing radiation (medium-energy electron beam) over these spent catalysts was studied to contribute the extraction of metals or rare-earths of high added-value. Tests conducted with HCC catalysts were used the technique of electron beam irradiation (1.3 MeV) and had as a subject the extraction of Molybdenum. Energy Dispersive X-ray (EDX) analysis was performed on a Shimadzu EDX-720/800HS and X-ray Diffraction (XRD) analysis on a Rigaku MultiFlex. Electron beam irradiation had a positive contribution if compared to traditional thermal and chemical methods. In temperature around 750°C, HCC irradiated catalysts of the lower region have an extraction of Molybdenum (MoO_3) yield twice higher compared to non-irradiated ones, in other words 57.65% and 26.24%, respectively.

Keywords: *Electron beam irradiation, Spent cracking catalysts, Extraction of Molybdenum, Hydro Catalytic Cracking (HCC), EDX and XRD analyses.*

1. INTRODUCTION

The Ni(Co)-Mo/Al2O3 catalyst is used in the crude-oil processing, in a stage called Hydro Catalytic Cracking (HCC). The use of HCC catalyst is an example of material that, after thoroughly characterized, became framed as hazardous waste from the late 90's. This situation was maintained in the review published by the Environmental Protection Agency (EPA) [1].

Radiation research applied to petroleum has been pursued by major oil companies, academia and national laboratories since the 1950's. Radiation in different forms (neutrons, electron beam, X-rays and gamma rays) can be delivered to petroleum crude oil to break large hydrocarbon molecules [2,3]. In this context there is a very important component: the catalyst. In the catalytic cracking process, the catalyst was designed to crack molecular chains, and as result a high residual carbon content called coke is deposited on catalyst surface [4,5].

When studying electron beam with medium and higher-energies is possible to induce the decomposition of supported Ni(Co)-Mo/Al2O3 sulfide catalyst and organic fragments of hydrogenation catalyst wastes and also recovery of noble materials such as Cobalt and Molybdenum, as well as, the study of catalyst impregnated with coke from the crude oil distillation on an industrial scale [6].

Ionizing radiations from gamma rays and electron beam would be then a “green chemical” approach to extract elements with high-added value such as Molybdenum from HCC catalyst and Lanthanum from FCC catalyst. Tests conducted with Fluid Catalytic Cracking (FCC) catalysts were used the techniques of Cobalt-60 irradiation and electron beam and had as a subject the extraction of Lanthanum [7,8].

1.1. Objective

The application of ionizing radiation from an industrial electron beam accelerator (1.5 MeV, 25 mA and 37.5 kW) over Hydro Catalytic Cracking (HCC) spent catalysts was studied to contribute the extraction of metals (Molybdenum) with high added-value.

2. MATERIALS AND METHODS

The Hydro Catalytic Cracking (HCC) catalyst is an extrudate with 4 mm to 8 mm in length and 2 mm to 5 mm in diameter. Three stages of HCC were studied: virgin and spent from upper and lower zones. Due to the heterogeneity of the catalyst, the Energy Dispersive X-ray (EDX) analysis was performed on a Shimadzu EDX-720/800HS in triplicate, as shown in Table 1.

Table 1. EDX analysis of Hydro Catalytic Cracking (HCC) catalyst: virgin and spent from lower and upper zones.

Oxides (%)	Virgin HCC	Spent HCC from lower zone	Spent HCC from upper zone
Al_2O_3	56.234±0.111	46.098±0.106	34.212±0.118
As_2O_3	-	0.017±0.005	0.828±0.009
CaO	0.084±0.003	0.119±0.003	0.339±0.005
Co_2O_3	0.026±0.003	0.018±0.003	0.045±0.005
Fe_2O_3	0.02±0.003	0.233±0.005	3.649±0.014
MoO_3	23.331±0.022	19.908±0.018	13.269±0.013
NiO	5.367±0.015	4.349±0.013	4.74±0.013
P_2O_5	4.063±0.022	4.241±0.024	3.29±0.029
SeO_2	-	-	0.006±0.001
SiO_2	0.006±0.016	0.128±0.021	8.88±0.046
SO_3	10.865±0.022	24.855±0.032	30.152±0.042
V_2O_5	0.001±0.007	0.027±0.008	0.546±0.011
ZnO	0.002±0.001	0.006±0.001	0.043±0.002

- Not detected.

To get an initial idea of the crystalline structure of the HCC catalyst, a sample was analyzed by X-ray Diffraction (XRD) analysis on a Rigaku MultiFlex, as shown in Figure 1. It is possible to understand that the catalysts do not have well-defined crystalline phases. Therefore, to evaluate the influence of electron beam irradiation on the catalyst, having as objective the extraction of Molybdenum, the EDX analysis results will be used to follow up the variation of the percentages of the elements of interest.

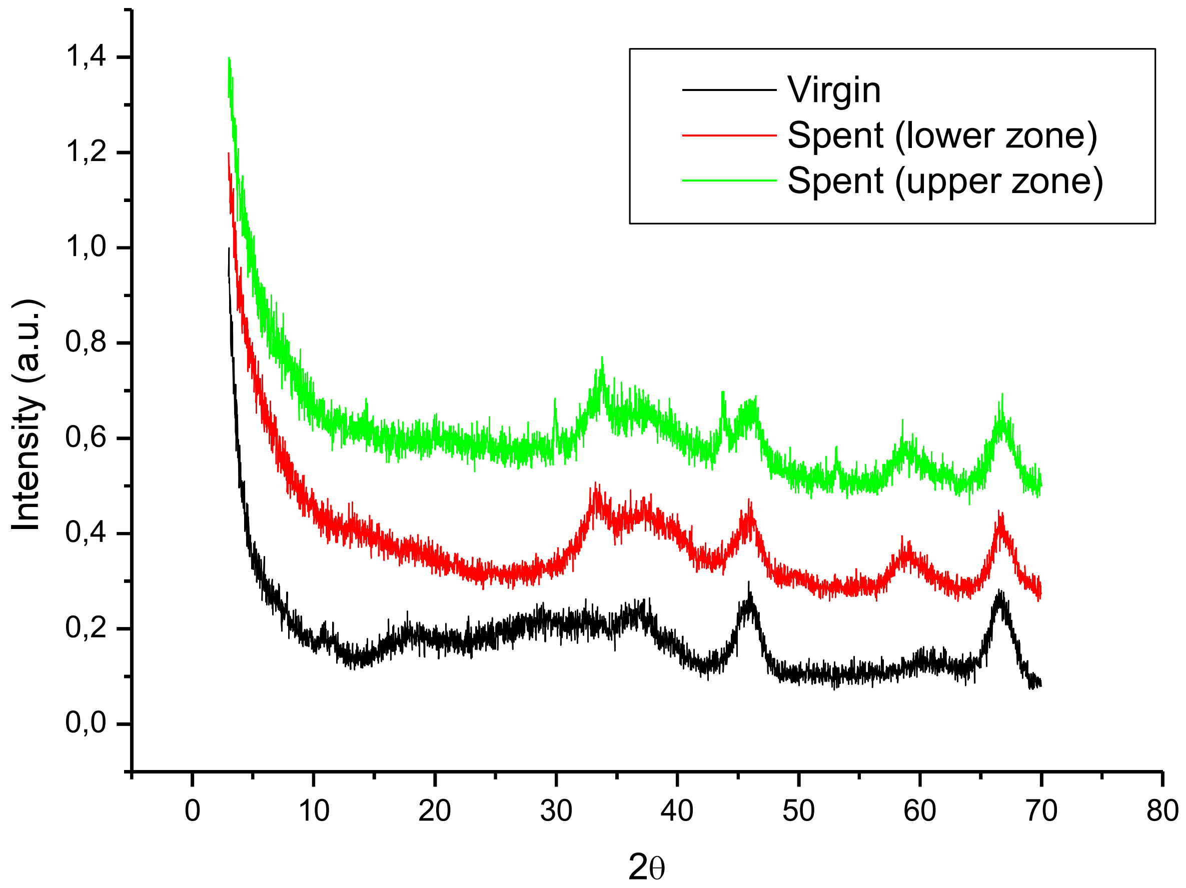

Fig. 1. Diffractogram comparison of Hydro Catalytic Cracking (HCC) virgin and spent (lower and upper zones) catalysts.

During the grinding process of the upper zone spent catalyst, spheres were found that were difficult to macerate. These spheres were washed with deionized water and dried, so no catalyst residue would be impregnated on its surface. After being cleaned the spheres were analyzed by X-ray Diffraction (XRD) analysis. Through the diffractogram shown in Figure 2, it is observed that this sphere is composed of α-alumina, and probably was not formed in the process but added to assist in the extraction of coke by mechanical crushing.

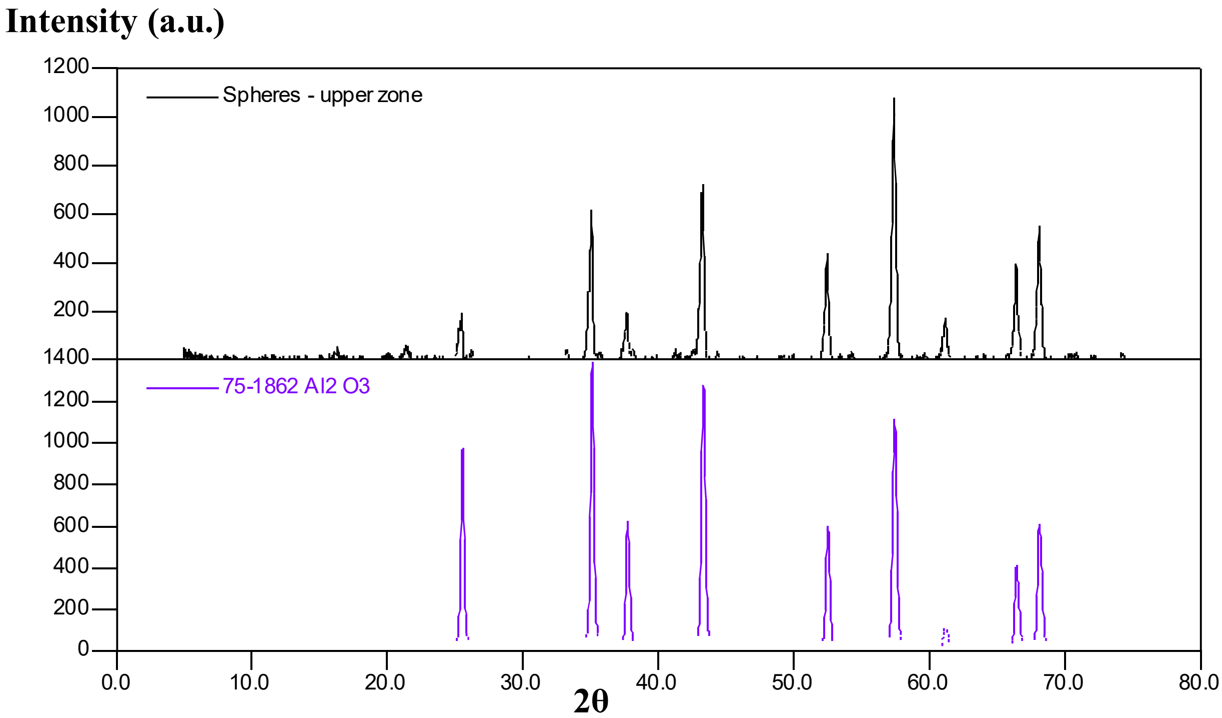

Fig. 2. Diffractogram of alumina-α spheres found in spent Hydro Catalytic Cracking (HCC) catalyst from upper zone.

The HCC catalyst has in its composition chemical elements with high-added value, which worth its extraction. So, methods that facilitate the extraction of those elements can make the whole process financially feasible. On top of that, the Hydro Catalytic Cracking (HCC) catalyst is considered hazardous waste**.**

2.1. Experimental

To make possible the understanding if the electron-beam irradiation allied with a thermal treatment would collaborate in the extraction of Molybdenum, the comparison between the methods was needed. So, to obtain the desirable information, the HCC catalyst was prepared in two distinct routes: Thermal-Treatment (TT) and Radiation-Thermal Treatment (RTT).

2.1.1. Thermal Treatment (TT)

In the Thermal Treatment (TT) route, the HCC catalyst was placed inside an alumina crucible, positioned on the heating device assembled on the Radiation Technology Center at IPEN-CNEN/SP, with the resistor of an X-ray diffractometer heating accessory ceded to the experiment. The resistor was connected to a variable transformer, which was connected to an alternating current.

The system was equipped with three multimeters. The first one for temperature control made by the thermocouple R-type (Pt-Rh filament of 13% with 0.2 mm in diameter). The millivolt scale was converted using the table for temperature conversion. The second calibrated multimeter, also for temperature control, made by a K-type thermocouple (chromel-alumel filament), obtaining the temperature directly in degrees Celsius. The last multimeter was used to follow the voltage applied to the system.

In Figure 3 is shown the heating system assembled for thermal treatment. In these tests, spent HCC catalysts were used, regarded as solid residue of the oil refining process.

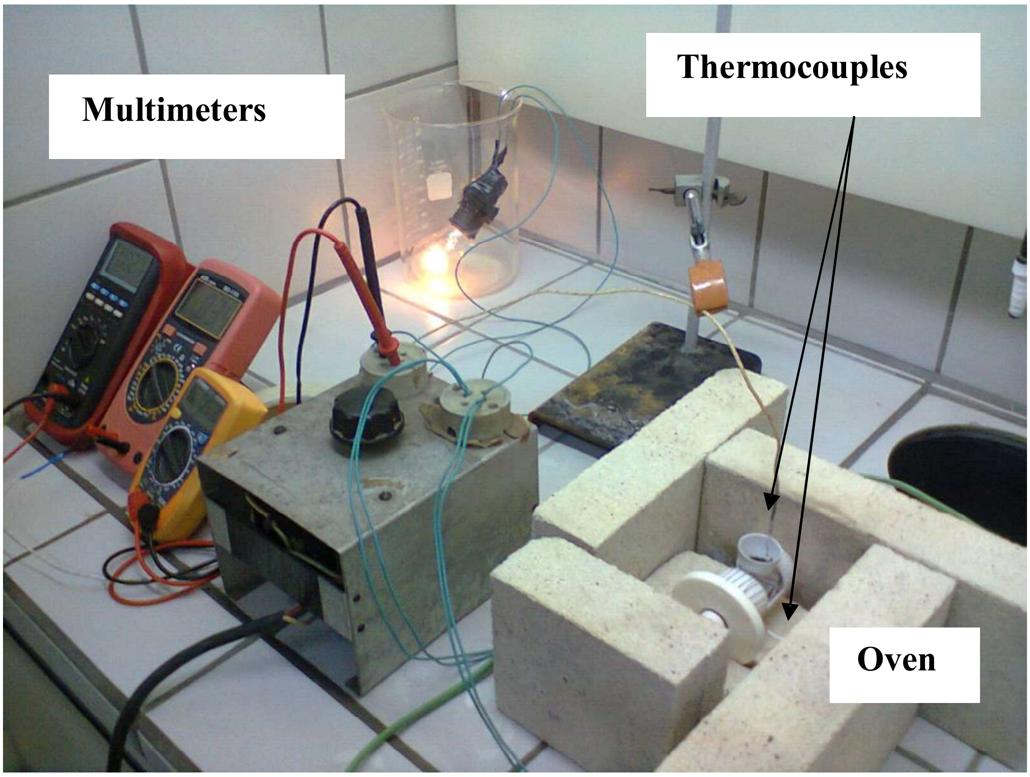

Fig. 3. Hydro Catalytic Cracking (HCC) catalyst heat system with temperature control.

Four trials were performed, two of them with the spent from lower zone and the other two with the spent from the upper zone. The spent HCC catalyst from the lower zone were heat treated in the average temperature of 747 °C (TT-1) and 650°C (TT-2), and the upper zone of 916°C (TT-3) and 1056°C (TT-4). Both catalysts were heat treated in the same heating system shown in Figure 3 for a period of 20 minutes.

After the heat treatment the catalyst was collected and cooled in desiccator, homogenized and submitted for Energy Dispersive X-ray (EDX) analysis. By comparing the EDX data before and after the heat treatment, the percentage of Molybdenum extracted was calculated.

2.1.2. Radiation-Thermal Treatment (RTT)

This essay concerns the thermal treatment with medium-energy electron beams irradiation. The catalyst was irradiated at room temperature using an industrial electron accelerator (1.5 MeV, 25 mA and 37.5 kW), Dynamitron DC 4/25/1500, JOB model 188, energy of 1.3 MeV, current of 3.5 mA at a dose rate of 25.3 kGy/s. The alumina crucible was exposed to the electron beam for 20 minutes of adding the final 30.36 MGy absorbed dose. In order to irradiate the Hydro Catalytic Cracking (HCC) catalysts samples, the heating system was positioned directly below the scan horn of the electron beam, as shown in Figure 4.

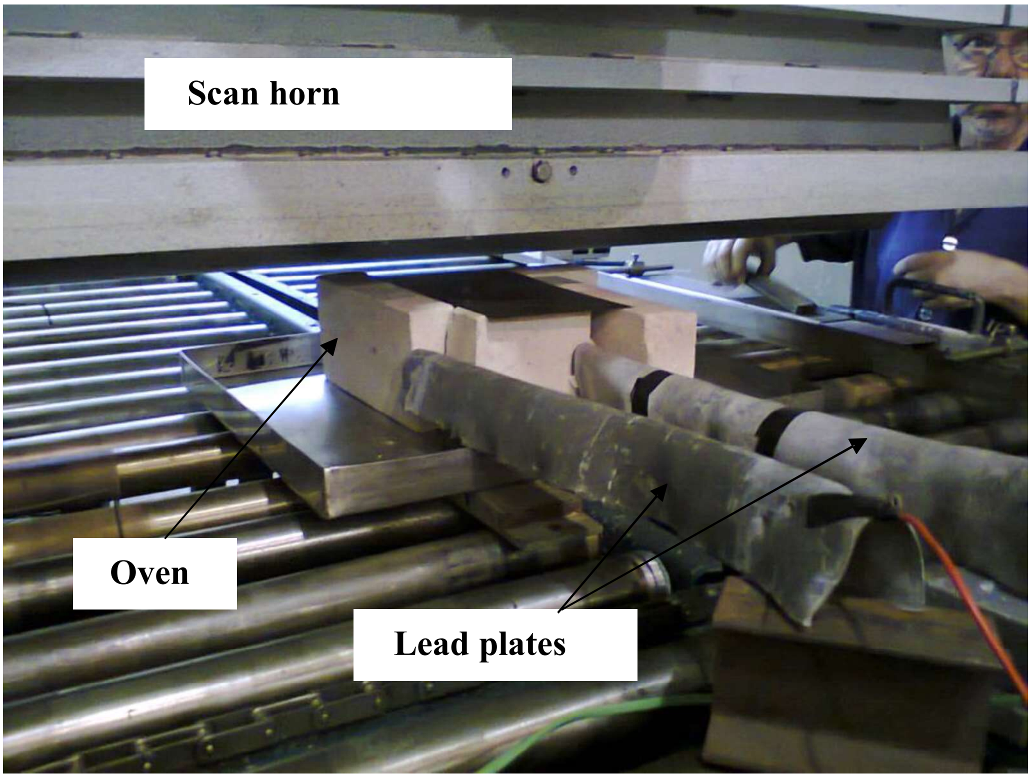

Fig. 4. Hydro Catalytic Cracking (HCC) catalyst radiation-thermal treatment system.

In order to the airflow that cools the cylinder head does not interfere with the heating, as well as the loss of catalyst from the crucible, the top of the heating system was covered with a thin titanium foil of 40 μm thickness by minimizing the attenuation of the incident electrons in the catalyst. This is the same material used on the electron accelerator window, which keeps the inner region in vacuum.

Electric and thermocouple compensating cables were covered with lead plates, ensuring no radiation interaction over the cable polymeric material (Figure 4). The heating system was the same used in the thermal treatment, with some modifications. First, the heating system was placed on a stainless steel AISI-304 tray so it could be easily handled. In this trial two multimeters were used, one to establish the voltage applied to the heating system and another to follow the temperature performed by an R-type thermocouple. After the voltage establishment in the system the multimeter was removed from the irradiation bunker. The temperature was real-time monitored from outside the installation.

As in the thermal treatment (TT), the radiation-thermal treatment (RTT) was performed four times, two with the spent HCC catalyst from lower zone and other two with spent HCC from upper zone. The spent HCC catalysts from lower zone were heat treated in the average temperature of 765°C (RTT-1) and 540°C (RTT-2), and the upper zone of 908°C (RTT-3) and 1058°C (RTT-4). After the heat treatment the catalyst was collected and cooled in desiccator, macerated and submitted for Energy Dispersive X-ray (EDX) analysis.

In both treatments (TT and RTT) temperature were obtained by the R-type thermocouple. However, this thermocouple is located much closer to the resistor compared to the sample. To obtain a more accurate temperature results a calibration curve was made using the K-type thermocouple as standard. This thermocouple was placed inside the crucible. A progressive heating was followed by both thermocouples. The calibration curve is shown in Figure 5.

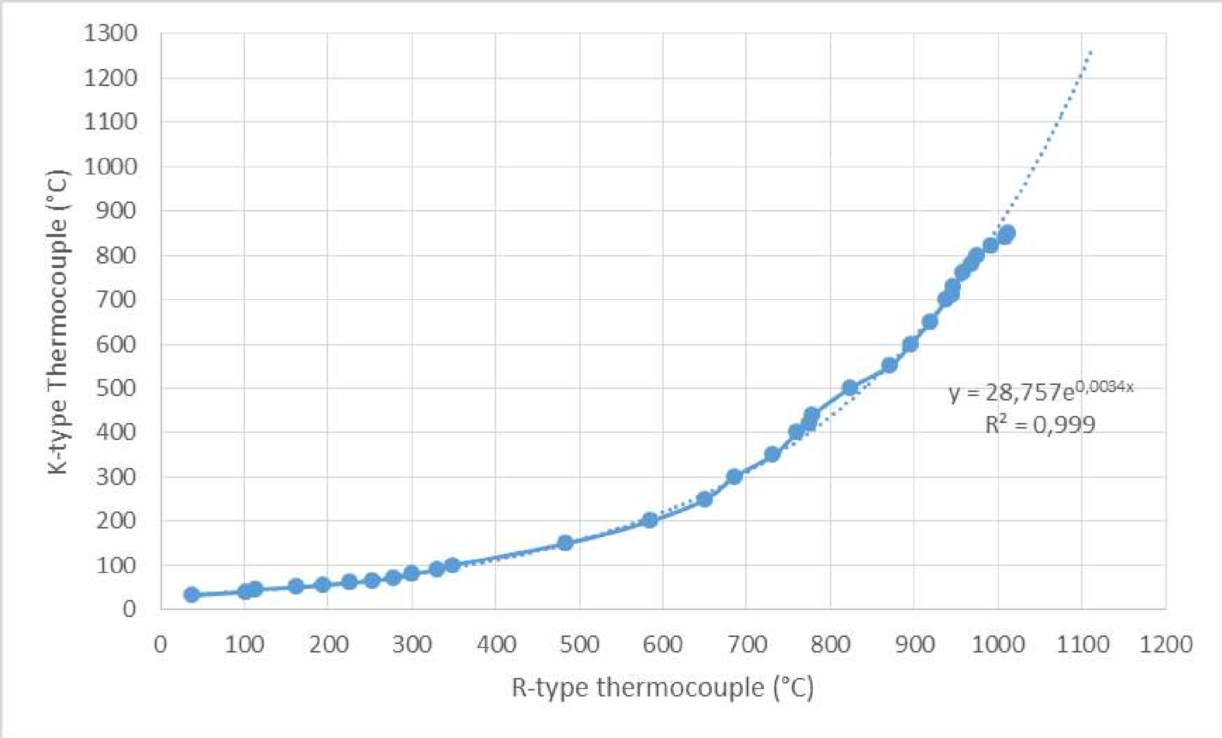

Fig. 5. Calibration curve for temperature measurement using the R-type and K-type thermocouples.

Having obtained the linear equation that best represents the curve profile generated by the temperature points; this equation was applied for the temperature values obtained by the R-type thermocouple, thus having the corrected temperature values.

3. RESULTS AND DISCUSSION

3.1. Thermal Treatment (TT)

After the temperature trial on the Hydro Catalytic Cracking (HCC) catalyst, the Energy Dispersive X-ray (EDX) analysis was performed in triplicate to study the yield of Molybdenum extraction. The results are shown in Table 2.

Table 2. EDX analysis of spent Hydro Catalytic Cracking (HCC) catalyst from lower and upper zones heat-treated.

Oxides (%)	Lower zone		Upper zone	
	TT-1	TT-2	TT-3	TT-4
Al_2O_3	56.274±0.107	60.421±0.111	48.324±0.112	50.133±0.114
As_2O_3	0.007±0.004	0.015±0.005	0.812±0.009	0.753±0.009
CaO	0.126±0.003	0.134±0.003	0.145±0.003	0.149±0.003
Co_2O_3	0.009±0.003	0.022±0.003	0.020±0.004	0.017±0.004
Fe_2O_3	0.192±0.004	0.191±0.004	1.325±0.009	1.279±0.009
MoO_3	17.926±0.016	19.952±0.018	18.292±0.017	17.855±0.017
NiO	4.334±0.012	4.955±0.014	4.448±0.013	4.590±0.013
P_2O_5	4.404±0.022	4.012±0.021	3.049±0.023	3.107±0.023
SeO_2	-	-	0.003±0.001	0.002±0.001
SiO_2	0.025±0.019	-	7.256±0.036	6.713±0.036
SO_3	16.692±0.025	10.271±0.021	15.815±0.027	14.924±0.027
V_2O_5	0.008±0.007	0.020±0.007	0.495±0.012	0.467±0.011
ZnO	0.004±0.001	0.004±0.001	0.016±0.001	0.010±0.001

- Not detected.

To calculate the efficiency of Molybdenum extraction it is necessary to calculate the mass overall balance. In this case, the aluminum oxide (Al_2O_3) was chosen as a standard element considering the heat treatment is not capable to extract it, since its boiling point is within 2980°C, much higher than used in the thermal treatment [9]. Using the Equation 1 it is possible to calculate the percentage of Molybdenum found in the sample and, consequently, the percentage of extraction performed by the heat treatment.

$$\frac{\left(\frac{MoO3}{Al2O3}\right) after}{\left(\frac{MoO3}{Al2O3}\right) before} \; x\, 100 \qquad (1)$$

For this reason the Equation 1 was used to calculate the Molybdenum extraction, obtaining 26.238% (TT-1), 23.537% (TT-2), 2.403% (TT-3) and 8.172% (TT-4).

3.2. Radiation-Thermal Treatment (RTT)

After the radiation-thermal treatment trial on the Hydro Catalytic Cracking (HCC) catalyst, the Energy Dispersive X-ray (EDX) analysis was performed in triplicate to study the yield of Molybdenum extraction. The results are shown in Table 3.

Table 3. EDX analysis of spent Hydro Catalytic Cracking (HCC) catalyst from upper and lower zones heat-treated and irradiated with electron beam.

Oxides (%)	Lower zone		Upper zone	
	RTT-1	RTT-2	RTT-3	RTT-4
Al_2O_3	70.951±0.116	59.589±0.113	51.544±0.112	52.960±0.114
As_2O_3	0.007±0.003	0.023±0.005	0.760±0.009	0.630±0.008
CaO	0.136±0.003	0.130±0.003	0.135±0.003	0.106±0.003
Co_2O_3	0.015±0.003	0.019±0.003	0.021±0.004	0.016±0.003
Fe_2O_3	0.213±0.004	0.200±0.004	1.212±0.009	0.882±0.008
MoO_3	12.979±0.012	19.840±0.018	18.922±0.018	18.907±0.018
NiO	5.354±0.012	4.935±0.013	4.621±0.013	4.634±0.013
P_2O_5	4.223±0.021	4.281±0.022	3.008±0.022	3.081±0.022
SeO_2	-	-	0.001±0.001	0.003±0.001
SiO_2	0.055±0.018	0.004±0.016	6.423±0.034	4.880±0.031
SO_3	6.043±0.016	10.969±0.022	12.902±0.024	13.536±0.025
V_2O_5	0.020±0.006	0.008±0.007	0.437±0.011	0.361±0.010
ZnO	0.004±0.001	0.003±0.001	0.013±0.001	0.005±0.001

- Not detected.

To understand the data obtained by EDX analysis in the radiation-thermal treatment and calculate the yield of Molybdenum extraction it was used the Equation 1, as applied for the thermal treatment. The electron beam bombardment raise the temperature up to 558 °C, therefore, the maximum temperature obtained is controlled by the heating system. For RTT the maximum temperature reached was 1058 °C. For this reason the Equation 1 was used to calculate the Molybdenum extraction, obtaining 57,642% (RTT-1); 22,904% (RTT-2); 5,348% (RTT-3) and 7,952% (RTT-4).

In Table 4, comparative values of Thermal Treatment (TT) and Radiation-Thermal Treatment (RTT) are shown. The graphics in Figure 1 compare the performance of Molybdenum extraction for TT and RTT of spent Hydro Catalytic Cracking (HCC) catalysts, from a lower zone.

Table 4. Comparative extraction values of TT and RTT on spent HCC catalyst.

Thermal Treatment		Molybdenum extraction (%)	Temperature (°C)		Molybdenum extraction (%)	Radiation-Thermal Treatment
Lower zone	TT-1	26.238	747	765	57.642	RTT-1
	TT-2	23.537	650	540	22.904	RTT-2
Upper zone	TT-3	2.403	916	908	5.348	RTT-3
	TT-4	8.172	1056	1058	7.952	RTT-4

The graphics in Figure 6 and Figure 7 compare the performance of Molybdenum extraction for thermal treatment (TT) and radiation-thermal treatment (RTT) on spent Hydro Catalytic Cracking (HCC) catalysts from lower and upper zones.

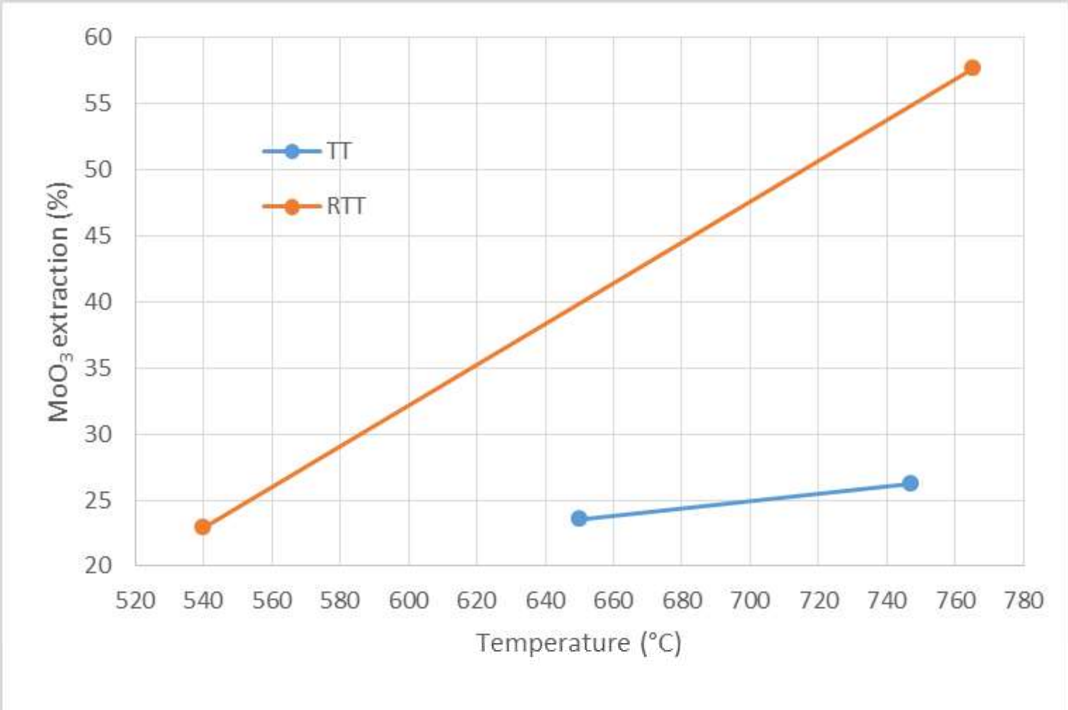

Fig. 6. Camparative extraction chart of thermal treatment (TT) and radiation-thermal treatment (RTT) on spent Hydro Catalytic Cracking (HCC) catalysts from lower zone.

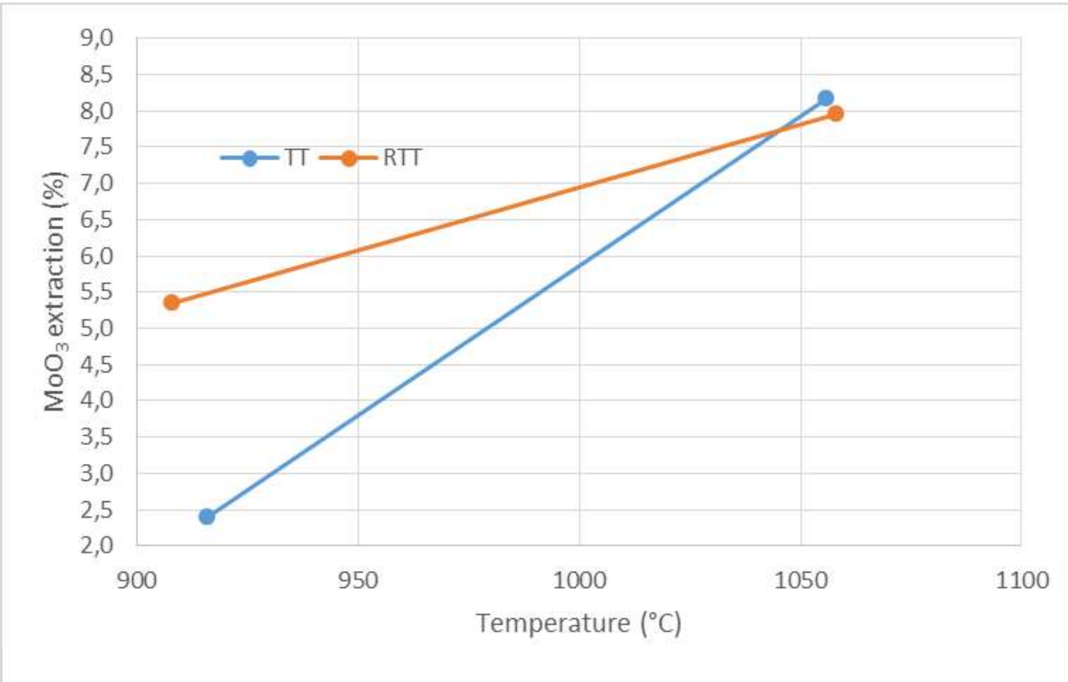

Fig. 7. Camparative extraction chart of thermal treatment (TT) and radiation-thermal treatment (RTT) on spent Hydro Catalytic Cracking (HCC) catalysts from upper zone.

It is possible to affirm that the electron beam (EB) irradiation gives support to the Molybdenum extraction in both cases. However, there is a great contrast for the spent catalyst from the lower zones once the higher the thermal energy applied, the greater the yield of extraction. For the spent catalysts from the upper zone, there is a higher yield of Molybdenum extraction at lower temperatures (900°C). At higher temperatures (1060°C), there is no contribution to the radiation.

During the radiation-thermal treatment (RTT-1), a crystal around the alumina crucible was observed, as shown in Figure 8. The crystal was removed and ground to be analyzed by X-ray Diffraction (XRD) analysis. The diffractogram is shown in Figure 9.

(a) (b)

Fig. 8. Radiation-thermal treatment (RTT) processing on spent Hydro Catalytic Cracking (HCC) catalyst from upper zone: a) alumina crucible and b) crystal formed after electron beam irradiation.

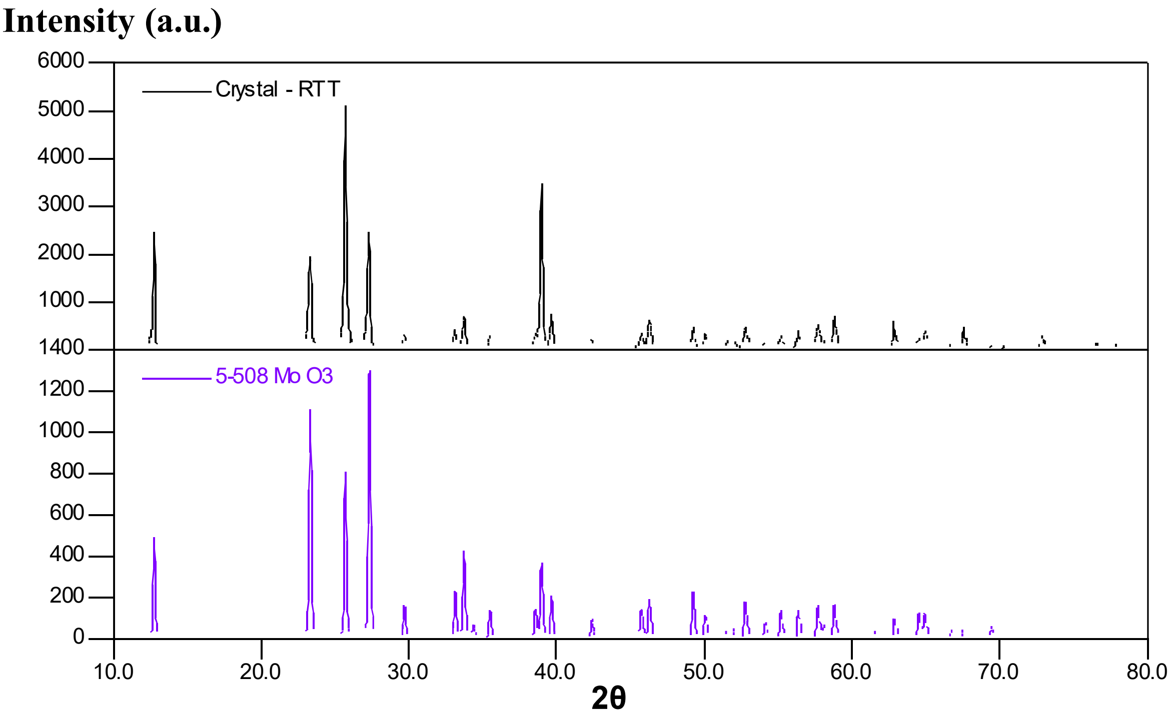

Fig. 9. X-ray diffractogram of the crystal formed in RTT processing on spent HCC catalyst, from a lower zone on a Rigaku MultiFlex.

The crystal formed in the radiation-thermal treatment (RTT-1) is Molybdenum Trioxide (MoO_3), extracted from spent HCC catalyst (lower zone). It is possible that the internal heat system conditions favored the recrystallization of MoO_3 crystal with 99.9% purity, in cooler parts of the apparatus assembled for the RTT experiment. On the other trials, there was a loss of molybdenum from the catalyst processed by the RTT and thermal Treatment (TT), but there was not recrystallization of Molybdenum. In the RTT, the medium-energy electron beam (1.5 MeV) reduces the temperature of vaporization of Molybdenum trioxide, making it possible its sublimation with greater efficiency. This is due to the crystallization of some phases that contain Molybdenum, which is readily destroyed by radiolysis, at high temperatures.

4. CONCLUSION

The irradiation of spent Hydro Catalytic Cracking (HCC) from a lower zone, with medium-energy (1.3 MeV) electron beam, current of 3.5 mA and dose rate of 25.3 kGy/s proves the efficiency regarding the extraction of Molybdenum (MoO_3). At similar temperatures, around 750°C, irradiated HCC catalysts showed a yield (57.65%) of two times as high, compared to those which were not irradiated (26.24%). For a spent HCC catalyst from an upper zone, the irradiation also proves efficiency, although, not as high as in spent HCC from a lower zone, and for high temperatures, around 1050°C, the participation of radiation is indifferent.

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