



Extraction of molybdenum from spent NiMo hydrocracking catalysts assisted by ionizing radiation

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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 and hydrocracking carried out with catalyst, 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 hydrocracking 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 analysis was performed on a Shimadzu EDX-720/800HS and X-ray Diffraction 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, hydrocracking irradiated catalysts of the lower region have an extraction of molybdenum (MoO₃) yield twice higher compared to non-irradiated ones, in other words 57.65% and 26.24%, respectively.

1. Introduction

The Ni(Co)–Mo/Al₂O₃ catalyst is used in the crude-oil processing, in a stage called hydrocracking (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) (Afonso et al., 2006).

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.

Processing high sulfur oils consumes HCC catalysts in large quantities. Despite the possible regeneration of hydrogenation catalysts based on Ni(Co) and Mo oxides, significant catalyst losses occur due to their irreversible deactivation. There are a wide variety of methods for extracting inactive components, such as aqueous and ammonia-aqueous

extraction of Mo, which allows the separation of Ni(Co) and Mo compounds, and the extraction of approximately 90% by mass of Mo in the form of MoO₃, and alkaline treatment (isolation of Mo up to 80% by mass), regardless of the initial concentration and structure of the compound. Complete purification of C and S oxides (up to 99% by mass) was first performed using the Radiation-Thermal Treatment (RTT) technique and the possibility of metal extraction by irradiation was noted by Solovetskii, Yu.I. "Problemy Dezaktivatsii Katalizatorov".

The radiation-induced decomposition by ionizing radiation of supported Ni(Co)–Mo/Al₂O₃ sulfide catalysts and organic fragments of hydrogenation catalyst wastes was also studied. The distribution of radiolysis products was studied as a function of time (up to 1 h) and temperature (297 °C to 1127 °C).

Experimentally, extrudates of Mo-containing catalyst samples (4 mm–8 mm in length by 2 mm–5 mm in diameter) with an initial composition of 4.9 wt% of Ni(Co), 12 wt% of Mo, 20 wt% of C, 5 wt% of S and remaining Al₂O₃ were subjected to the RTT technique at 1.2 MeV of beam energy, using an industrial electron accelerator built by the

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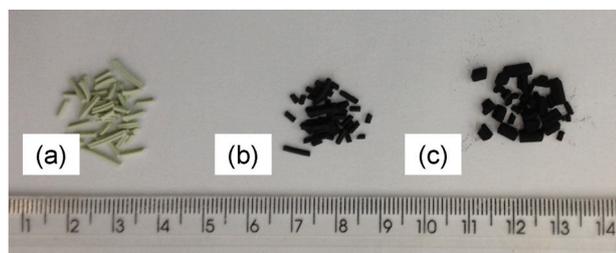


Fig. 1. HCC catalyst: a) virgin; b) spent from upper zone; and c) spent from lower zone.

Table 1
EDX analysis of HCC catalyst: virgin and spent from lower and upper zones.

Oxides (%)	Virgin HCC	Spent HCC from lower zone	Spent HCC from upper zone
Al ₂ O ₃	56.234 ± 0.111	46.098 ± 0.106	34.212 ± 0.118
As ₂ O ₃	–	0.017 ± 0.005	0.828 ± 0.009
CaO	0.084 ± 0.003	0.119 ± 0.003	0.339 ± 0.005
Co ₂ O ₃	0.026 ± 0.003	0.018 ± 0.003	0.045 ± 0.005
Fe ₂ O 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 ₂ O 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 ₂ O 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.

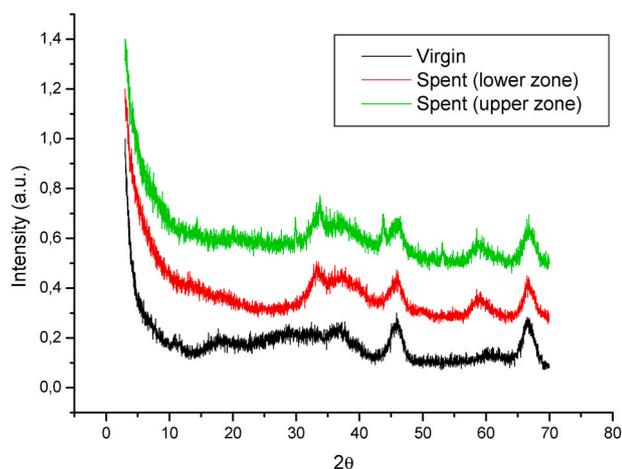


Fig. 2. Diffractogram comparison of HCC virgin and spent (lower and upper zones) catalysts.

Institute of Nuclear Physics, Siberian Branch, Russian Academy of Sciences. The result for the RTT (electron beam irradiation of up to 2.0 MeV, in 30 min) in the deactivated Ni(Co)-Mo/Al₂O₃ was similar to the conventional heat treatment between 540 °C to 650 °C (Lunin et al., 1993; Solovetskii et al., 1998).

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 (Guisnet et al., 2009; Mitchell, 1980).

When studying electron beam with medium and higher-energies it 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 refining on an industrial scale (Lima et al., 1998).

Ionizing radiations from gamma rays and electron beam (EB) 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 (Binnemans et al., 2013; Kondo et al., 2016).

1.1. Objective

The application of ionizing radiation from an industrial Electron Beam Accelerator - EBA (1.5 MeV, 25 mA and 37.5 kW) over HCC spent catalysts was studied to contribute the extraction of metals (molybdenum) with high added-value.

2. Materials and methods

The HCC catalyst is an extrudate with 4 mm–8 mm in length and 2 mm–5 mm in diameter. In three stages of the HCC process, industrial catalysts have been studied: virgin catalyst, spent catalyst from upper zone and spent catalyst from lower zone, as shown in Fig. 1.

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.

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 Fig. 2. 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.

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 XRD analysis. Through the diffractogram shown in Fig. 3, 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.

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 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 RTT.

2.1.1. Thermal treatment

In the 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

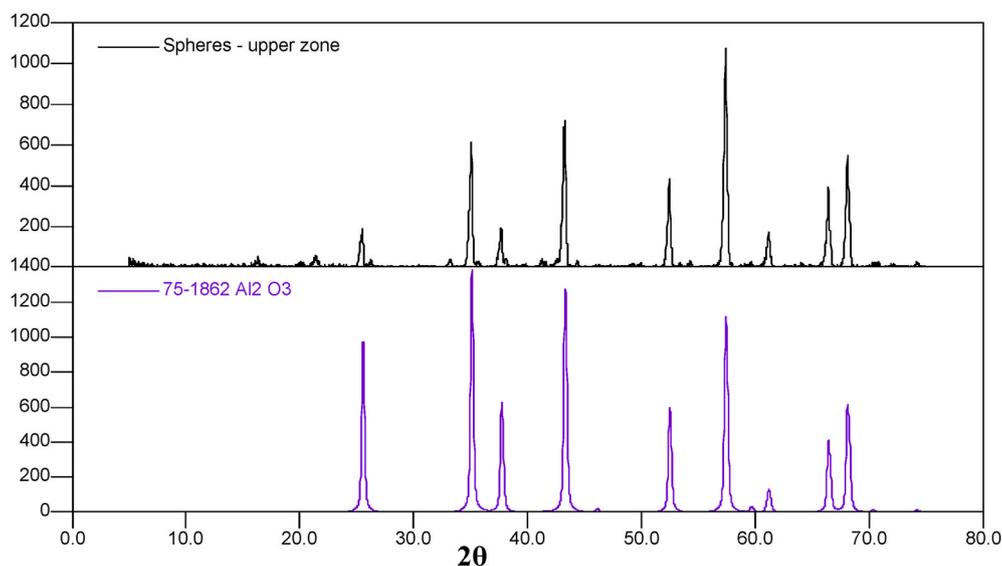


Fig. 3. Diffractogram of alumina- α spheres found in spent HCC catalyst from upper zone.

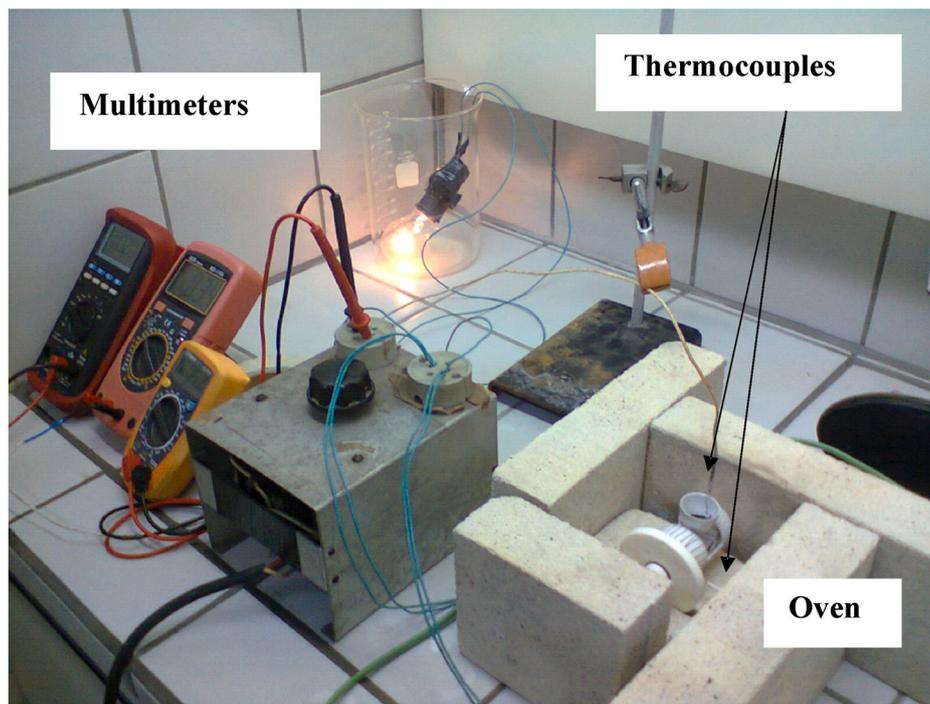


Fig. 4. HCC catalyst heat system with temperature control.

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 Fig. 4 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.

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 Fig. 4 for a period of 20 min.

After the heat treatment the catalyst was collected and cooled in desiccator, homogenized and submitted for 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

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 min of adding the final 30.36 MGy absorbed dose. In order to irradiate the HCC catalysts

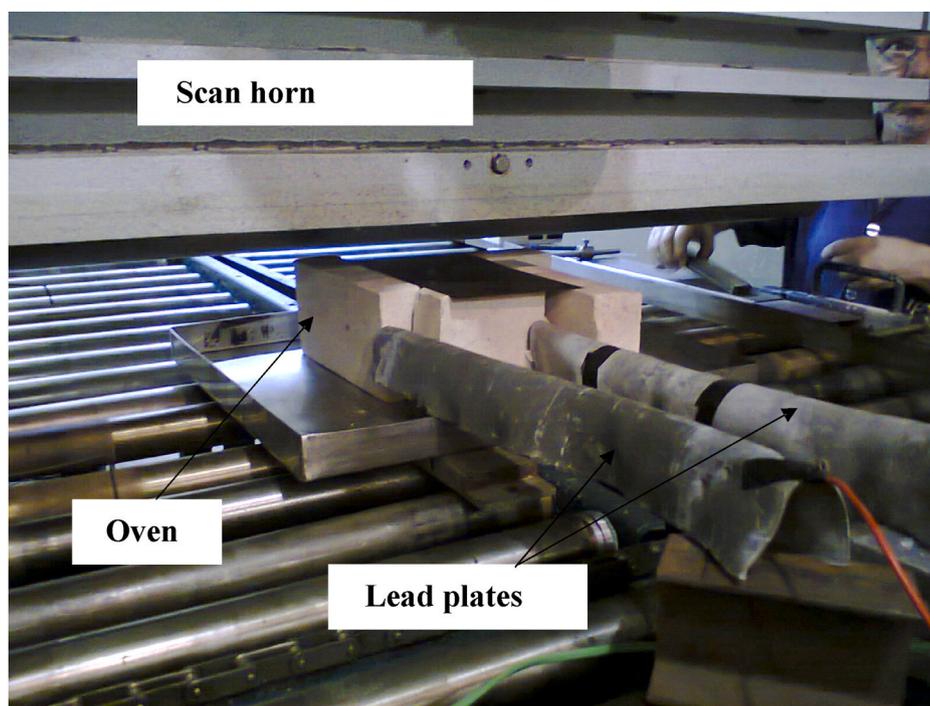


Fig. 5. HCC catalyst in the RTT system.

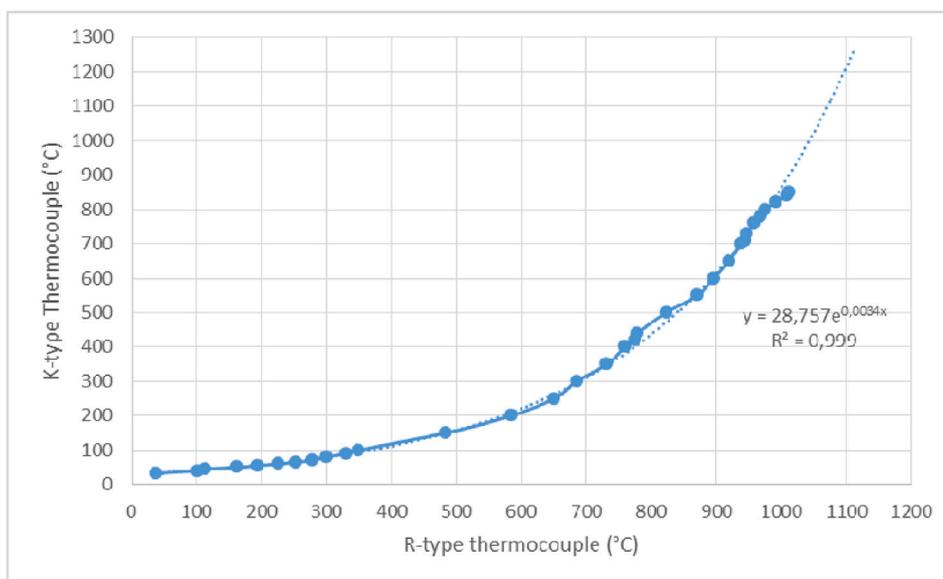


Fig. 6. Calibration curve for temperature measurement using the R-type and K-type thermocouples.

samples, the heating system was positioned directly below the scan horn of the electron beam, as shown in Fig. 5.

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 (Fig. 5). 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 TT, the 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 $^{\circ}\text{C}$ (RTT-1) and 540 $^{\circ}\text{C}$ (RTT-2), and the upper zone of 908 $^{\circ}\text{C}$ (RTT-3) and 1058 $^{\circ}\text{C}$ (RTT-4). After the heat treatment the catalyst was collected and cooled in desiccator, macerated and submitted for EDX analysis.

In both treatments (TT and RTT) temperatures were obtained by the

Table 2
EDX analysis of spent HCC catalyst from lower and upper zones heat-treated.

Oxides (%)	Lower zone		Upper zone	
	TT-1	TT-2	TT-3	TT-4
Al ₂ O ₃	56.274 ± 0.107	60.421 ± 0.111	48.324 ± 0.112	50.133 ± 0.114
As ₂ O 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 ₂ O ₃	0.009 ± 0.003	0.022 ± 0.003	0.020 ± 0.004	0.017 ± 0.004
Fe ₂ O 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 ₂ O 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 ₂ O 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.

Table 3
EDX analysis of spent 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 ₂ O ₃	70.951 ± 0.116	59.589 ± 0.113	51.544 ± 0.112	52.960 ± 0.114
As ₂ O 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 ₂ O ₃	0.015 ± 0.003	0.019 ± 0.003	0.021 ± 0.004	0.016 ± 0.003
Fe ₂ O 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 ₂ O 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 ₂ O 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.

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

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 Fig. 6.

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

After the temperature trial on the HCC catalyst, the EDX analysis was performed in triplicate to study the yield of molybdenum extraction. The results are shown in Table 2.

To calculate the efficiency of molybdenum extraction it is necessary

to calculate the mass overall balance. In this case, the aluminum oxide (Al₂O₃) 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 TT (Sigma-Aldrich, 2019). Using 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.

$$\left(\frac{\text{MoO}_3}{\text{Al}_2\text{O}_3} \right)_{\text{after}} \times 100 \quad (1)$$

For this reason 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

After the RTT trial on the HCC catalyst, the EDX analysis was performed in triplicate to study the yield of molybdenum extraction. The results are shown in Table 3.

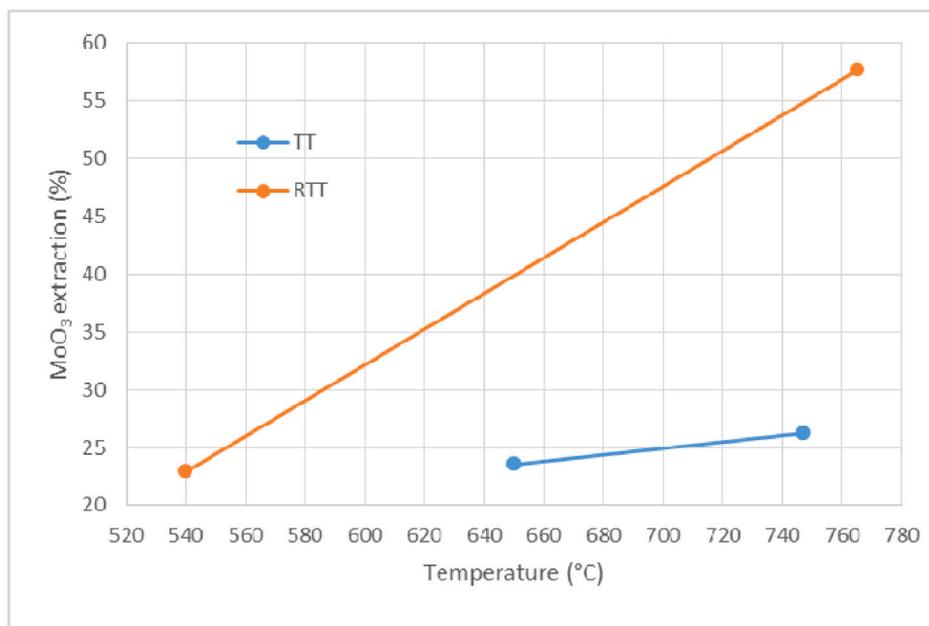


Fig. 7. Comparative extraction chart of TT and RTT on spent HCC catalysts from lower zone.

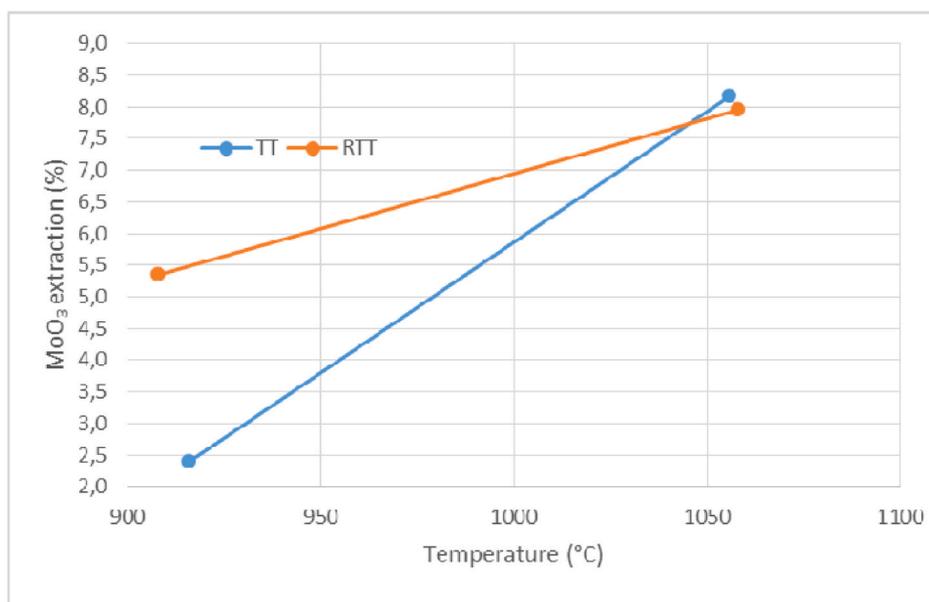


Fig. 8. Comparative extraction chart of TT and RTT on spent HCC catalysts from upper zone.

To understand the data obtained by EDX analysis in the RTT and calculate the yield of molybdenum extraction it was used 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 Equation (1) was used to calculate the molybdenum extraction, obtaining 57,642% (RTT-1); 22,904% (RTT-2); 5348% (RTT-3) and 7952% (RTT-4).

In Table 4, comparative values of TT and RTT are shown.

The graphics in Fig. 7 and Fig. 8 compare the performance of molybdenum extraction for TT and RTT on spent HCC catalysts from lower and upper zones.

It is possible to affirm that the electron beam 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 RTT-1, a crystal around the alumina crucible was observed, as shown in Fig. 9. The crystal was removed and ground to be analyzed by XRD analysis. The diffractogram is shown in Fig. 10.

The crystal formed in the 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 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



Fig. 9. RTT-1 processing on spent HCC catalyst from lower zone: a) alumina crucible and b) crystal formed after electron beam irradiation.

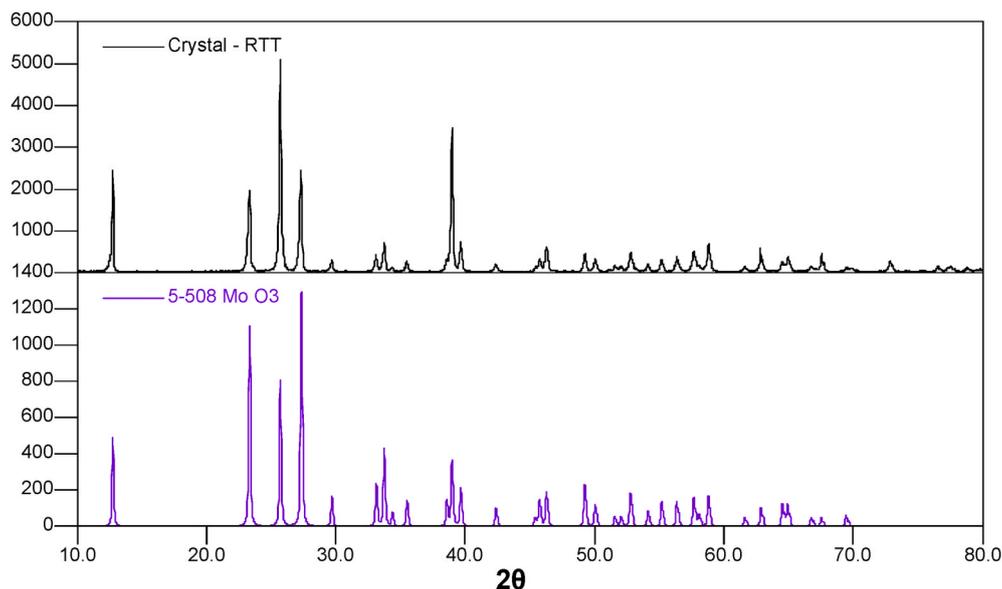


Fig. 10. X-ray diffractogram of the crystal formed in RTT processing on spent HCC catalyst, from a lower zone on a Rigaku MultiFlex.

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 HCC catalyst 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 (57.64%) 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.

Declaration of competing interest

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

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