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Analysis of Petroleum Oily Sludge Produced from Oil-Water Separator

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Análise de Borra Oleosa de Petróleo Proveniente do Separador Água e Óleo

Resumo: As borras oleosas são formadas durante as operações de produção, transporte, armazenamento e na refinaria de petróleo. A análise elementar foi realizada com amostras de borra oleosa de petróleo coletadas no Estado do Rio Grande do Norte. Para o elemento carbono e o hidrogênio foram observadas pequenas diferenças entre os mesmos, mas para o elemento oxigênio foram observadas diferenças maiores entre as amostras de borra. As mesmas apresentaram diferenças na composição química da parte inorgânica e orgânica. A borra do separador água e óleo (SAO) 2 apresentou uma elevada quantidade de óleo (94,88%), essa pode ser considerada um resíduo de elevado valor agregado para a indústria de petróleo. Nas análises de saturados, aromáticos, resinas e asfaltenos (SARA), a borra do descarrego apresentou uma elevada quantidade de saturados. O material inorgânico separado da borra do SAO 2 foi caracterizado e apresentou muito enxofre (41,57 %). As borras analisadas apresentaram elevado valor de componentes orgânicos, logo esse material pode ser tratado e reprocessado em unidades de processos na indústria de petróleo.

Palavras-chave: Borra Oleosa; Petróleo; Degradação; Resíduo; Meio Ambiente.

Abstract

The petroleum oily sludge is formed during the production, transportation, and storage processes as well as in the oil refinery plant. The elemental analysis was performed with samples of petroleum oily sludge collected in the State of Rio Grande do Norte. For the carbon and hydrogen elements, small differences were observed between them, but for the oxygen element, bigger differences between the sludge samples were noticed. They have presented differences in the chemical composition of inorganic and organic parts. The sludge from oil-water separator (OWS) 2 showed a high amount of oil (94.88%), being considered a high value-added residue by the oil industry. In the analyses of saturated, aromatics, resins, and asphaltenes (SARA) components, the sludge from the unloading had a high amount of saturates. The inorganic material separated from the sludge of the OWS 2 was characterized, and presented a lot of sulfur (41.57 %). The sludge analyzed showed a high value of organic components, thus such material can be handled and reprocessed in processing units within the oil industry.

Keywords: Oily Sludge; Petroleum; Residue; Waste; Environment.

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Analysis of Petroleum Oily Sludge Produced from Water-Oil Separator

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1. Introduction

The residues generated in Brazilian regions have different characteristics and they are marked by economic and industry development factors. Different solid waste is generated in the petroleum exploration and production.[1,2] The petroleum oily sludge is a complex mix of different components (water, oil and solid).[3] The petroleum oily sludge generally and other residues are generally formed during the production, operation, transport, storage, and refining of oil (atmospheric residue, vacuum residue, and catalytic cracking residue).[4] However, according with the origin, the compositions of 30 – 50% of oil or 30 – 50% of water can be found quite varied.[5] By observing the production and refining process steps it is possible to locate its main sources and percentage contributions in terms of waste generation. The petroleum oily sludge can be considered a solid waste of great sisgnificance in the petroleum and gas industry.[6,7] Those petroleum residues from the bottom of storage tanks, oil-water separators (OWS), desalted oil systems, or catalytic cracking units[8,9,10] vary widely in composition, and because of the high toxicity, they cannot be discarded, but they can be processed with other wastes generated. The OWS operates continuously, as the effluent enters the OWS, the solids are retained at the bottom of the equipment, the oil is separated from the OWS, and the effluent is released to meet the standards required by legislation. The solid waste is composed primarily of sand particles with oil and those should be treated accordingly.[11,12] The oily residues on the surface of the OWS should be tank mixed with diesel or fuel oil unit, if it is possible to reuse it. The oily sludge had been until a very recent past, stored in tanks or disposed of in landfills, so almost randomly, even in developed countries, due to the lack, until then of a more specific legislation.[13] The protection of the environment taking place through the reduction or elimination of solid waste generated, which would be incinerated or land filled generating possible contamination.[14] The waste can also be co-processed contributing to power generation and a considerable environmental liability.[15,16] The use of solid waste has become a matter of great importance in the national and international context. There are different examples, which can be cited with the management of Class I solid waste, classified as one of the most dangerous.[17] Some ways of reusing that waste as oily sludge and other wastes are through catalytic and thermal treatment.[18,19,20] The aim of this study is to characterize the different type of petroleum waste (sludge) and its thermocatalytic decomposition.

2. Materials and Sources

2.1. Soxhlet Extraction of Petroleum Oily Sludge

A soxhlet system was used in the chemical extraction, the oily sludge was put in cartridges of filter paper, and transferred to the soxhlet apparatus.[21] The instrument consists of an extractor tube, flask of flat bottom, and a condenser. The extractor tube was connected to a flask containing the solvent chloroform. The flask was heated by a heater plate at specific temperatures of 145°C, the solvent evaporated, condensing in the condenser, where the droplets fall on the cartridges and store until the reflux. The process is repeated until all sludge was separated into the organic and inorganic material, shortly thereafter, a part of the solvent was recovered. After such process, the oil was stored in appropriate containers for further analysis and inorganic part.

2.2. Elemental Analysis Petroleum Oily Sludge

The composition of the oily sludge and Vacuum Residue (VR) was obtained with an elemental analyzer,[22] EACHNS-O 1110, Thermo Quest CE Instruments brand, from approximately 3mg of sample, using helium as carrier gas at 130mL/min. and O_2 burning gas at 300mL/min. The reactor temperature was 1000°C and the run time of 420 seconds on the synthetic air.

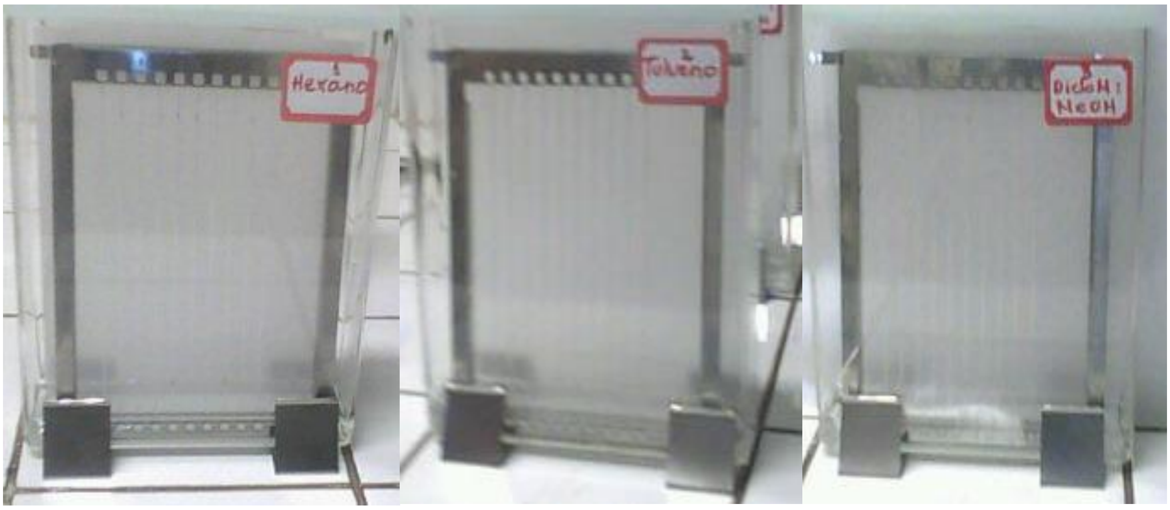
2.3. Analysis of Saturates, Aromatics, Resins and Asphaltenes (SARA) of Petroleum Oily Sludge and X-Ray Fluorescence (XRF)

The chemical extraction was performed on a system of hexane, the solvent chloroform. This system was separated by organic components (oil) and inorganic components (sand particles). In this, oils obtained were analyzed through thin layer chromatography for the quantification of oil fractions: saturates, aromatics, resins, and asphaltenes (SARA), and an analysis X-Ray Fluorescence (XRF)[23] was done in the inorganic materials sample obtained.[23] We used the technique of thin layer chromatography with flame ionization detector (TLC/FID), the Iatroscan combines the techniques of TLC (Figure 1), an established technique for the separation of organic compounds (petroleum fraction). The samples were weighed (0.1g), and diluted with 10mL of dichloromethane. The diluted samples were filtered in milipore filters (0.45m) (Figure 2). The spot of filtered samples was performed with an amount of 1.0µL (Figure 3). After spot, the syringe was washed six times before using another sample. 60mL of each of the elution solvent in vats (vat 1 – hexane, vat 2 – toluene) were placed in different vats. Vat third in 60mL solvent, a solvent mixture in a proportion (dichloromethane and methanol – 57:3) was also placed. The metal support with rods was placed inside vat 1 (hexane), and left to elute for 40 minutes. The metal support with rods was removed from the vat and placed in vat 2 (toluene), and left to elute up to 60cm (measurement scale in metallic form) was then taken to the oven for 2 minutes (Figure 4). The metal support with rods was placed in vat 3, left to elute up to 25cm, brought to the oven and to the thin layer chromatographic with flame ionization detector instrument. The instrument operates with a flame formed by hydrogen gas (H_2), and a flow rate of 160-170mL/min. The technique used for determining the sample analysis of the inorganic chemical element was in the form of compacted pellets. The equipment used was the EDX-900, produced by Shimadzu Corporation. The operating parameters of spectrometer were the ray tube X Rhodium, voltage of 5KV, current automatically adjusted in most 1mA, collimator of 10mm, silicon detector, cooling thermocouple, measurement time of 40 seconds, and 8 for scans per analysis. A support for solid sample of polystyrene film was used.

Figure 1. Chromatography System with Flame Ionization Detection

Figure 2. Filtration Process with Millipore Filters

Figure 3. Metalic Suport for spotation of Samples



a) b) c)

Figure 4. a) Vat with Hexane, b) Vat with Toluene, c) Vat with Dichlomethane and Methanol

2.4. Analysis Thermogravimetric of Petroleum Oily Sludge from Unloading

A sample 10 milligram of petroleum oily sludge was used in thermal degradation.[24-26] A sample of 10 milligram (mg) of oily sludge was used in thermal degradation analysis. The Analysis was carried out in the thermogravimetric equipment with thermobalance Mettler-SDTA 851, in temperature range of 30 – 900°C, under flowing helium (100 $mL.min^{-1}$), and a heating rate of 10°C $.min^{-1}$.

3. Results and Discussion

3.1. Elemental Analysis Petroleum Oily Sludge

Tables 1-4 present the elemental analysis results of petroleum oily sludge. It was observed that all sludges do not have sulfur in their composition in this analysis. Table 1 presents oily sludge that was collected in the discharge system and it has different mixture sludges from oil-water separators. Tables 2, 3 and 4 show sludge from oil-water separator of different petroleum field production in the same region. These latest results showed higher concentration of the carbon element, with exception of sludge presented in Table 4. The petroleum oily sludge examined from the oil-water separator presented in Table 3, showed less Oxygen and Nitrogen element. This sludge may indicate a small quantity of resins and asphaltenes, a small number of heteroatom in its composition.

Table 1. Elemental Analysis Oily Sludge from Unloanding

Element	% Weight
Carbon	85.20
Hydrogen	10.93
Oxygen	3.62
Nitrogen	0.25

Table 2. Elemental Analysis Oily Sludge from OWS 1

Element	% Weight
Carbon	87.07
Hydrogen	11.12
Oxygen	1.59
Nitrogen	0.22

Table 3. Elemental Analysis Oily Sludge from OWS 2

Element	% Weight
Carbon	87.14
Hydrogen	11.24
Oxygen	1.46
Nitrogen	0.16

Table 4. Elemental Analysis Oily Sludge from OWS 3

Element	% Weight
Carbon	85.68
Hydrogen	9.46
Oxygen	3.88
Nitrogen	0.20

3.2. Analysis of Saturates, Aromatics, Resins and Asphaltenes (SARA) of Petroleum Oily Sludge

Tables 5, 6, 7 and 8 show chemical composition data of petroleum oily sludge from unloading and OWS of petroleum wells in the state of Rio Grande do Norte. It was shown in Table 5, that such type of oil has a higher percentage of saturated compounds, it showed a greater area in the chromatographic analysis. It can be considered a solid waste with high commercial value for having that amount of compounds considered mild. The resins are composed of cycles that can be used in petrochemicals, considered of great interest in the oil industry. Table 6 presents data collected from OWS sludge, can be observed that the fractions are different petroleum in Table 5. The sludge in Table 5 presents a characteristic of mild oil with lower percentage of saturated and consequently a greater amount of heavy fraction, in this case, the asphaltene fraction. Tables 7 and 8 show another type of sludge composition in other oil-water separators. A smaller amount asphaltene fraction was shown in Table 7, but for this type of sludge a greater amount of aromatic fraction was observed. A greater number of resins fraction was observed in Table 8, with little difference between the other fractions.

Table 5. Data relating to petroleum oily sludge collected from unloading

Fraction	Retention time (s)	Height	Area	Area (%)
Saturated	0.033	6.098	15.168	51.93
Aromatics	0.235	1.980	5.207	17.83
Resins	0.361	9.863	7.046	24.12
Asphaltenes	0.466	2.271	1.784	6.11

Table 6. Data relating to petroleum oily sludge collected from the water-oil separator 1

Fraction	Retention time (s)	Height	Area	Area (%)
Saturated	0.021	7.363	14.163	34.69
Aromatics	0.238	4.136	8.364	20.49
Resins	0.353	18.055	12.292	30.11
Asphaltenes	0.471	8.045	6.000	14.71

Table 7. Data relating to petroleum oily sludge collected from the water-oil separator 2

Fraction	Retention time (s)	Height	Area	Area (%)
Saturated	0.051	11.277	2.784	4.67
Aromatics	0.258	20.917	41.005	68.75
Resins	0.358	17.780	11.213	18.80
Asphaltenes	0.468	5.852	4.645	7.79

Table 8. Data relating to petroleum oily sludge collected from the water-oil separator 3

Fraction	Retention time (s)	Height	Area	Area (%)
Saturated	0.008	3.358	5.656	19.10
Aromatics	0.251	4.613	8.194	27.67
Resins	0.356	14.511	10.794	36.45
Asphaltenes	0.466	5.578	4.967	16.78

3.3. Elemental Analysis of Organic and Inorganic Components in Petroleum Oily Sludge

The petroleum oily sludge from unloading was extracted in system Soxhlet and presented in its composition 74.45% organic components (oil) and 25.55% inorganic components (oxides and salts) were analyzed by XRF analysis in Table 9. This analysis was also performed for another sample of sludge and water-oil separator (WOS) 1, showed 65.92% organic components (oil) and 34.08% inorganic components, showed in Table 10. The Table 11 and 12 show results of petroleum oily sludge collected in WOS 1 and 2. The sludge from WOS 2 showed 94.88% organic components (oil) and 5.12% inorganic components (Table 11). The sludge from

WOS 3 showed 69.72% organic components and 30.28% inorganic components (Table 12). All samples presented Sulfur element in your composition after the Soxhlet extraction test. The samples analyzed in Tables 11 and 12 showed higher amounts of Sulfur element. The sludge originates from unloading showed low amount Sulfur element (Table 9). The Sulfur element has been separated during extraction of sludge (Sohxlet extraction process) and in elemental analysis (Table 1, 2, 3 and 4) did not show presence of sulfur component in composition of petroleum oily sludge after your extraction. The Nickel element was found in 3 samples (Table 10, 11 and 12), it is considered a heavy metal. The sample collected in WOS 2 (Table 10) showed greater amount Nickel element (heavy metal).

Table 9. Inorganic elemental analysis part contained in petroleum oily sludge from unloanding

Parameter	Result (%)	Parameter	Result (%)
Aluminum	6.09	Magnesium	1.13
Calcium	21.71	Potassium	2.21
Chlorine	3.55	Silicon	25.07
Sulfur	1.62	Sodium	1.77
Iron	36.84		

Table 10. Inorganic elemental analysis part contained in petroleum oily sludge from WOS 1

Parameter	Result (%)	Parameter	Result (%)
Aluminum	7.32	Phosphorus	0.38
Calcium	7.91	Magnesium	1.62
Copper	5.70	Nickel	23.45
Chlorine	5.10	Potassium	1.93
Sulfur	12.46	Silicon	11.16
Iron	19.68	Sodium	3.26

Table 11. Inorganic elemental analysis part contained in petroleum oily sludge from WOS 2

Parameter	Result (%)	Parameter	Result (%)
Aluminum	1.32	Nickel	4.03
Barium	28.98	Silicon	6.36
Calcium	12.84	Sodium	1.68
Sulfur	41.57		
Iron	3.22		

Table 12. Inorganic elemental analysis part contained in petroleum oily sludge from WOS 3

Parameter	Result (%)	Parameter	Result (%)
Aluminum	1.23	Nickel	5.95
Barium	32.25	Potassium	0.53
Calcium	19.81	Silicon	3.75
Sulfur	32.87	Sodium	1.09
Iron	3.51		

3.4. Analysis Thermogravimetric of Petroleum Oily Sludge from Unloading

It was observed in the oily sludge sample collected that there is a large amount of sand, and that other contaminants have not been identified, they influenced negatively in its thermogravimetric (TG) characterization. The raw and treated samples are shown in Figures (5 and 6), which present the thermal analysis of petroleum oily sludge. In Figure 5, the regions of distillation and thermal cracking were not observed clearly, events are disorganized, which can be attributed to different contaminants in raw sludge. Figures 6, 7, 8 and 9, show the thermogram of oily sludges after the filtration process, and it could be observed that the distillation and cracking regions were well defined. A greater degradation was observed in Figure 7 in the region of 300°C (distillation region), and almost all their products were left at this temperature. The degradation in Figure 8 occurred at 300°C, but a small amount of products above 400°C. In Figure 9, it was observed that a sludge has been degraded at temperatures of 300°C and above 400°C.

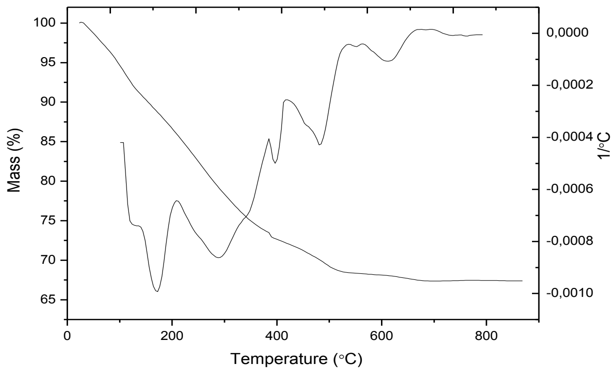


Figure 5. TG and DTG raw petroleum oily sludge unloading

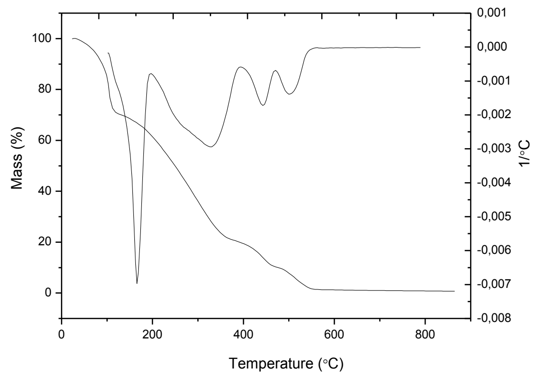


Figure 6. TG and DTG Analysis of petroleum oily sludge unloading filtered from Soxhlet

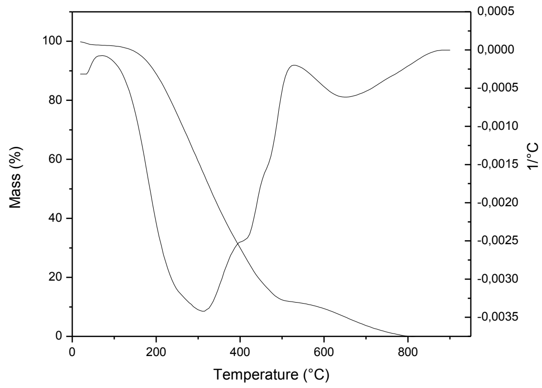


Figure 7. TG and DTG Analysis of petroleum oily sludge WOS 1

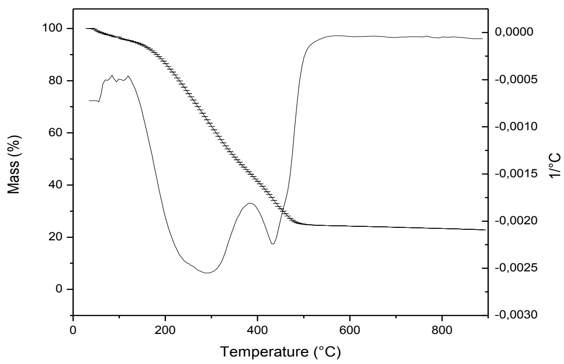


Figure 8. TG and DTG Analysis of petroleum oily sludge WOS 2

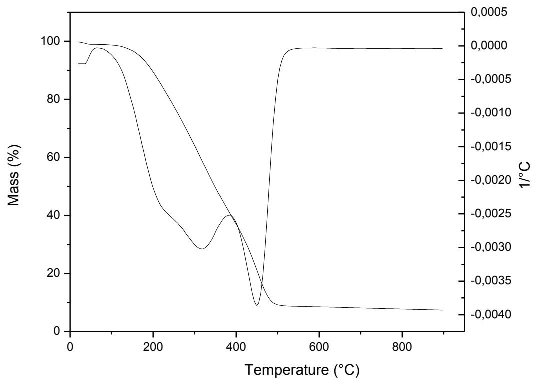


Figure. 9. TG and DTG Analysis of petroleum oily sludge WOS 3

4. Conclusions

The petroleum oily sludge showed different organic and inorganic components in all analysis carried out. The system was efficient in soxhlet extraction process for organic and inorganic components present in all oily sludge. That residue showed a high amount of oil and small heavy metals were found in XRF analysis, which can be considered a residue of high aggregate value. A positive factor was found for such waste, which showed a high percentage of Resins and Saturated, being compared to other fractions in the sludge analyzed. Different types of sludge can show different compositions for the organic and inorganic part, the composition varied with the sludge type and petroleum origin. The sludge analyzed showed heavy metal in its composition (inorganic part), Nickel was the heavy metal found in the sludge. In the thermogravimetric analysis, well defined events for the sludge treated degradation were found, and a suggested presence of compounds (gasoline, fuel oil, and diesel oil) could be observed in the region of 300 °C to 450 °C. The Petroleum oily sludge from oil and water separation 1 showed higher degradation at lower temperature, so it can show lighter fractions in its composition.

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