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Petroleum Refinery Oily Sludge: The Quantitative And Qualitative Analysis Of Its Composition

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Abstract:Refinery oily sludge is one of the major sludge generated from the petroleum refineries. The quantity of sludge generated by the refineries is huge and is going to scale up further in future as the demand for petroleum product keeps on growing. The composition of oily sludge is very complex. It comprises of a mixture of petroleum hydrocarbons, asphaltenes, long chain paraffinic wax, waste water, sediments and metals. Refinery sludge comes under the hazardous category. It has become an important environmental and public health issue in India and disposal of excess sludge will be forbidden in the near future Moreover as the crude reserves is depleting our refiners are aimed to extract as much valuables as possible from the crude and from the left over sludge before disposing it.This research work is aimed to analyse the composition of the refinery oily sludge. The insight in the composition of refinery oily sludge will facilitate therefiners to find a way for improving the recovery of valuables from oily sludgeand foreconomical, fast and eco-friendly disposal of treated sludge.

Keywords: Asphaltenes, composition of sludge, metals, refineryoily sludge,wax

INTRODUCTION

Crude oil is an important source of energy and is also a common source of environmental pollution [21]. One of the consequences of crude oil exploitation and processing activities is the generation of vast amounts of oily sludge[16].Petroleum refineries unavoidably generate a huge amount of sludge during their storage operations andthrough on-going operations. The major sludge generated by the petroleum refineries are oily sludge,bio-sludge and chemical sludge[15].Most of the crude oils have a property to separate into the heavier and lighter hydrocarbons during their storage and transportation. Also during lifting, transportation and processing of oil, emulsions and sludge are formed. Eighty percent of these oil/water emulsion is of water-in –oil emulsions type [17][4].The heavy ends that separate from the crude oil are found to get deposited on the bottoms of the storage tanks/vessels, commonly known as tank bottoms or oily sludge. Oilysludgeis usually generated in refineries duringthe cleaning up of crude oil storage tanks, maintenanceof associated facilities and pre-export processing i.e. tank farms, desalter failure, oil draining from tanks andoperation units andpipeline ruptures [12].Among all the generated sludge, oily sludge is generated in much higher quantity than any other sludge [15]. In 2010-11 refineries in USAsludge generation was about 0.06% of total crude oil processed[11].Three to five percent of all crude oil produced is ultimately unusable as sludge [18].If we see in Indian scenario, HPCL refineriesprocessed 14.8MMT crude oilin year 2010-11and oily sludge generation was 2907 MT which is about 0.0196% of the total crude processed [22], BPCL refineries generated about 7000 MT of sludge which is about 0.03 % of total processed crude in 2009-10 [23],IOCL processed 52.962 MMT of crude and generated about 11,500MT of sludge which is 0.021% of total processed crude in the year 2010-11[24]. The processing activities of one kilogram of crude oil can generate 10-20 grams of oily sludge [10]. A total of 204.8 MMT crude oil was processed by Indian refineries in 2011-12[13]. Considering the average generation rate of sludge as 0.023% of the total processed crude, which is the average generation rate of IOCL, BPCL and HPCL, about 47000MT of sludge is generated in India in 2011-12.

The composition of oily sludge is very complex, generally it comprises of oil-water emulsion and suspended solids [3]. The composition of oily sludge varies due to the large diversity in the quality of crude oils, differences in the processes used for oil–water separation, leakages during industrial processes and also mixing with the existing oily sludge.Oily sludge is a combination of hydrocarbons, sediment, precipitates, paraffin and water[1][20].These precipitates were mainly asphaltenes, resins, paraffin waxes and other poly-aromatic hydrocarbons [25].The Ministry of Environment and Forests, Government of India has categorized refinery oily sludge as the hazardous waste and it has become an important environmental and public health issue in India, like other developed and developing countries [19].Becauseof the hazardous nature of oily sludge, disposal of excess sludge will be forbidden in the near future, thus increased attention has been turned to look into potential technology for sludge treatment. Even bioremediation for disposal of sludge was found slow for some refineries for instancein the case study at Mangalore refinery, the time for bioremediation was more than 20 months and the rate of biodegradation of TPH was 0.07 Kg TPH/day/m2 area of bioremediation site [2].India is the fifth largest energy consumer in the world. There is a growing demand as a result of the rise in population and economic growth. Demand is also fuelled by increasing industrialization and usage of gas in these industries. India's petroleum product consumption has grown by 4-5% over the past 10 years and the oil demand in India is expected to rise to 368 MMTPA by 2025 [5]. And also as the crude reserves is depleting our refiners cannot afford to waste any valuable in the form of sludge and are aimed to extract as much valuables as possible from the crude and from the left over sludge before disposing it .Thus refiners have two major agenda for sludge treatment.Firstly is to improve the recovery of valuables from oily sludge and secondly to find a way for economical, fast and eco-friendly disposal of treated sludge. The insight in the composition of refinery oily sludge will facilitate the refiners to find the means to improve the recovery of valuables from oily sludge andalso determining the composition of the sludge is an important step in finding the way for economical, fast and eco-friendly disposal of the treated sludge. An analysis to determine the composition of the sludge is an important step in determining the most efficient means to remove it. The research work is aimed to analyze the composition of the refinery oily sludge both quantitative and qualitative.

2. STUDY AREA

The Mangalore Refinery and Petrochemicals Limited (MRPL), Mangalore, Karnataka, India was chosen as focal point for study. MRPL is one of the best operating refineries in India and it processes a very large number of crudes and thus the sludge sample will represents the typical oily sludge generated by a typical refinery across India.

3. OBJECTIVE OF STUDY

The main objective of the study is to analyze the oily sludge sample collected from different location of the refinery for its qualitative and quantitative composition so as to give an insight for the future researcher to find the best possible method to recover the valuable from the sludge and for disposal of the sludge in eco-friendly ways.

4. MATERIALS ANDMETHODS

4.1. Materials

The oily sludge sample used for this study was collected from the crude tanks, FB7001B and FB7001G, during manual tank cleaning process and from ETP sludge pit of Mangalore Refinery and Petrochemicals Limited (MRPL), Mangalore.The solvents used in our study are toluene,n-heptane,acetone, petroleum spirit, sulphuric acid and Fuller's earth.

4.2. Methods

Oily sludge is a mixture of different kinds of hydrocarbons, water, sediments and suspended materials. The following fractions of sludge in the samples collected from the three location i.e. FB7001B (Sample A), FB7001G (Sample B) and from ETP sludge pit (Sample C) were analyzed as follows.

4.2.1Analysis of water content

Water content was measure as perASTM - D95method, American Standard for Testing and Materials[6]. In thismethod sample is heated under reflux with a water-immiscible solvent (toluene), which co-distils with water in the sample. Condensed solvent and water is continuously separated in a trap, the water settles in the graduation section of the trap and the solvent returns to the still.

4.2.2Analysis for the sediments

The test method used for the determination of the sediments in the sample is ASTM D473, American Standard for Testing and Materials [7]. The sample of known mass was taken in the dried thimble and sediment is extracted using hot toluene by heating under reflux.

4.2.3Analysis for asphaltenes content

The analysis for asphaltenes is based on method ASTM D6560, American Standard for Testing and Materials[8]. For the analysis a test portion of the sample is mixed with n-heptane and the mixture is heated under reflux, the resultant precipitated asphaltenes, waxy substances, and inorganic materials are collected on the filter paper. The waxy substances are removed by washing with hot heptane in an extractor. After removal of waxy substances, the asphaltenes are separated from the inorganic materials by dissolution in the hot toluene, the extraction solvent is subsequently evaporated, and the asphaltenes are weighed.

4.2.4Analysis for wax content

The analysis for wax is based on method IS: 10512-1983, Indian standard methods [14]. Sample of known mass containing wax is dissolved in petroleum spirit and clarified using Fuller's earth and is then filtered. The petroleum spirit is evaporated and the clarified oil is re-dissolved in acetone-petroleum spirit. This solution is then cooled to-18°C using chiller and the crystallized wax is filtered using petroleum spirit. The spirit is evaporated and the wax is weighed.

4.2.5 Analysis ofvolatile or light hydrocarbon content

The oily sludge is mainly composed of water, sediments and other heavier components like wax and asphaltenes and the lighter hydrocarbon. As water, sediment, asphaltenes and wax content was measured previously in accordance with methods ASTM D95, ASTMD 473, ASTM D6560 and IS: 10512-1983 respectively. The light hydrocarbon content (in wt. %) was calculated as follows:

Light hydrocarbon (wt. %) =[1 – ((water content wt. %) + (sediment content wt. %)+(asphaltenes content wt. %)+ (waxcontent wt. %))]

4.2.6Metal Analysis of the residue

The residue after the sludge treatment is mainly composed of asphaltenes/wax and sediments. It also contains heavy metals in the significant amount. A study of heavy metal in the residue gives an insight into the possible methods of safe disposal/treatment of the oily sludge and its recovery so as to get pure wax/asphaltenes.

The methods used for the analysis of the metal are:
1.Flame Photometric Method(D1318-00) [8]
2.Atomic Absorption Spectrometry (UOP 391-91) [26]

Flame Photometric Method (D1318-00):This test method is used for the determination of sodium in crude residue. In this method a weighed sample is reduced to a carbonaceous ash. The residual carbon is removed by heating in a muffle furnace at 550°C.The ash is dissolved, diluted to volume, and the sodium determined by means of a flame photometer.

Atomic Absorption Spectrometry (UOP 391-91): This method is used for the determination of trace concentration of iron, nickel, vanadium by atomic absorption spectrophotometry. In this method the sample is wet ashed with fuming sulphuric acid and the resulting coke is oxidized in a muffle furnace. The inorganic residue remaining is dissolved in a mixture of acids and diluted. The sample solution is aspirated into the flame of an AAS instrument and quantification is achieved by comparison to the matrix-matched standard solutions.

5. RESULTS AND DISCUSSIONS

5.1Analysis for the water content

The analysis results for the sample A (Tank FB7001B), sample B (Tank FB7001G) and sample C (ETP sludge pit) are tabulated in Table 1, 2, 3 respectively.

Table 1: Water content in sample A

Weight of sample(g)	Water,%(v/v)
2.051	53.632
2.045	51.345
2.034	53.555
2.038	53.974
2.001	52.474

Table 2: Water content in sample B

Weight of sample (g)	Water, %(v/v)
2.057	52.906
2.015	52.591
3.012	53.441
2.152	54.762
2.485	53.338

Table 3: Water content in sample C

Weight of sample (g)	Water, %(v/v)
2.042	58.766
2.005	59.850
3.003	59.940
1.985	57.935
2.052	58.480

Average water content %,(v/v) in the sample was found to be 52.996 for sample A, 53.407 for sample B and 58.994 for sample C. The water content of sample C was found to be maximum as expected since it was drawn from Effluent Treatment Sludge pit.

5.2Analysis for the sediments

The analysis results for sample A (Tank FB7001B), sample B (Tank FB7001G) and sample C (ETP sludge pit) are tabulated in Table 4, 5, 6 respectively.

Table 4: Sediment content in sample A

Weight of sample(g)	Sediment,%(w/w)
10.7277	9.2625
10.1249	9.5020
10.1250	9.8324
10.0082	9.3204
9.8947	9.1505

Table 5: Sediment content in sample B

Weight of sample(g)	Sediment,%(w/w)
10.8014	10.365
10.1450	9.1993
9.8991	10.9147
10.0082	10.3814
10.0457	10.8693

Table 6: Sediment content in sample C

Weight of sample(g)	Sediment,%(w/w)
10.0014	7.9355
9.9885	8.1256
9.8845	7.6085
10.0571	8.0163
10.0045	8.2133

Average sediment content %,(w/w) in the sample was found to be 9.4135 for sample A, 10.3459 for sample B and 7.9798 for sample C.

5.3 Analysis for asphaltenes content

The analysis results for sample A (Tank FB7001B), sample B (Tank FB7001G) and sample C (ETP sludge pit) are tabulated in Table 7, 8, 9 respectively.

Table 7: Asphaltenes content in the sample A

Weight of sample(g)	Asphaltenes %(w/w)
0.8969	1.8843
0.9125	1.7863
1.0125	1.9753
0.9845	1.7877
1.0012	1.8877

Table 8: Asphaltenes content in the sample B

Weight of sample(g)	Asphaltenes, %(w/w)
0.9196	2.2183
0.9256	2.1175
1.0254	2.2138
0.9894	2.2539
1.0256	2.3011

Table 9: Asphaltenes content in the sample C

Weight of sample(g)	Asphaltenes, %(w/w)
0.9186	1.6438
0.9825	1.6183
1.0025	1.7257
0.9812	1.7020
0.9912	1.6445

Average asphaltenes content %,(w/w) in the sample was found to be 1.8642 for sample A, 2.2209 for sample B and 1.6669 for sample C.

5.4Analysis for wax content

The analysis results for sample A (Tank FB7001B), sample B (Tank FB7001G) and sample C (ETP sludge pit) are tabulated in Table 10, 11 12 respectively.

Table 10: Wax content in the sample A

Weight of sample(w1),g	Wax % ,(w/w)
2.5084	6.9287
2.8475	7.9683
2.4856	6.9359
2.5012	7.6848
2.7845	7.2221

Table 11: Wax content in the sample B

Weight of sample(w1),g	Wax % ,(w/w)
2.5010	16.2607
2.4561	15.9858
2.5612	14.9098
2.3256	14.8407
2.1456	15.8320

Table 12: Wax content in the sample C

Weight of sample(w1),g	Wax % ,(w/w)
2.3850	8.8553
2.4516	8.2028
2.5123	8.3986
3.4562	8.7188
2.7894	8.9661

Average wax content %,(w/w) in the sample was found to be 7.3479 for sample A, 15.5658 for sample B and 8.6283 for sample C. The tank FB7001B mostly stores Mumbai High crude which is waxy in nature and the analysis results also shows that the sludge sample B i.e. obtained from FB7001B is having wax % more than 10 and is waxy in nature.

5.5Analysis for volatile or light hydrocarbon content

The analysis results for sample A (Tank FB7001B), sample B (Tank FB7001G) and sample C (ETP sludge pit) are tabulated in Table 13, 14, 15 respectively.

Table 13: Oil content in the sample A

Water, %(w/w)	Sediment, %(w/w)	Wax, %(w/w)	Asphaltenes, %(w/w)	Oilcontent, %(w/w)
53.632	9.2625	6.9287	1.8843	28.2925
51.345	9.5020	7.9683	1.7863	29.3984
53.555	9.8324	6.9359	1.9753	27.2824
53.974	9.3204	7.6848	1.7877	28.7331
52.474	9.1505	7.2221	1.8877	28.1857

Table 14: Oil content in the sample B V

Water, %(w/w)	Sediment, %(w/w)	Wax, %(w/w)	Asphaltenes, %(w/w)	Oil content, %(w/w)
52.906	10.365	16.2607	2.2183	18.2500
52.591	9.1993	15.9858	2.1175	20.1064
53.441	10.9147	14.9098	2.2138	18.5207
54.762	10.3814	14.8407	2.2539	17.7620
53.338	10.8693	15.8320	2.3011	17.6596

Table 15: Oil content in the sample C

Water, %(w/w)	Sediment, %(w/w)	Wax, %(w/w)	Asphaltenes, %(w/w)	Oil content, %(w/w)
58.766	7.9355	8.8553	1.6438	22.7994
59.850	8.1256	8.2028	1.6183	22.2033
59.940	7.6085	8.3986	1.7257	22.3272
57.935	8.0163	8.7188	1.7020	23.6279
58.480	8.2133	8.9661	1.6445	22.6961

Average volatile or light hydrocarbon content %,(w/w) in the sample was found to be 28.3784 for sample A, 18.4597 for sample B and 22.7308 for sample C. The analysis results depicts the opportunity for recovery of oil from the sludge.

5.6Metal Analysis of the residue

The methods used for the analysis of the metal are:
1.Flame Photometric Method(D1318-00)
2.Atomic Absorption Spectrometry (UOP 391-91)

Flame Photometric Method (D1318-00): Analysis results: Sodium, mg/kg= 63ppm.

Atomic Absorption Spectrometry (UOP 391-91): Analysis results: Vanadium: 204ppm; Fe: 0.6%, Nickel: 506ppm

The results of the analysis of the sample A, B and C for its composition as illustrated in section 5 is compiled in Fig 1.The results clearly shows that sludge contains a considerable amount of light hydrocarbon in a significant amount of which can be recovered.

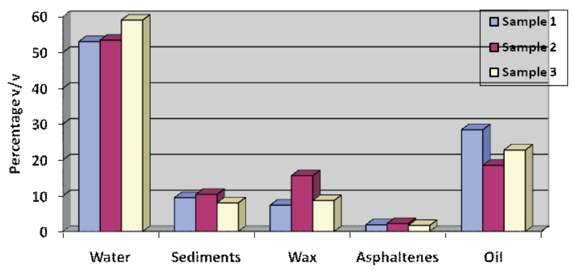

Figure1: Composition of the sludge samples

6. CONCLUSION

The major sludge generated in the refinery is oily, bio and chemical sludge. At present in India twenty two refineries are in operation which contribute significantly to sludgegeneration. Sludge usually contains various pollutantssuch as hydrocarbons, heavy metals etc. and uncontrolleddisposal ofsludge on land and in lagoons leads to severe environmentalpollution. After the introduction of the Hazardous Wastes (Handling & Management) Rules, industries aremore concerned with the sludge management problem andare in search of environmentally friendly solutions.Investigations of the constitution of the oily sludge sample revealed that a typical refinery sludge contains 55.13 ± 6.60 % of water content, 9.246 ± 13.6 % of sediments content, 1.9173 ± 15.8 % of asphaltenes content,10.514 ± 48.67 % of wax content and 23.19 ± 2.23 % of light hydrocarbons content.The higher concentration of heavy metals in high concentrations for instance vanadium is 204ppm, Fe is 0.6% and nickel is 506ppmmakes the oily sludge to be very harmful for the environment and organisms which need to be dealt with for environmental protection. The study of composition of the sludge clearly shows that sludge contains valuables like wax, asphaltenes and other hydrocarbon in the significant amount and gives the refiners an opportunity to recover these valuables to increase their refinery profit margins and also the amount of sludge disposal can be reduced significantly if the valuables like wax, asphaltenes and other hydrocarbon are recovered.

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