Chapter 5 Physicochemical characteristics of hazardous sludge from effluent treatment plant of petroleum refinery as feedstock for thermochemical processes

Abstract

The physicochemical characteristics of hazardous oily petroleum sludge (OPS) become reasonably important when it is used as feedstock in thermochemical processes for energy generation. Present work aimed at investigating the physicochemical characteristics of PS before and after Soxhlet extraction. Soxhlet extraction was performed using petroleum ether, hexane, toluene, and benzene as a solvent, among which hexane yields a maximum amount of liquid. Therefore, PS before and after solvent extraction using hexane was characterized using proximate, ultimate, TGA/DTG/DTA, FTIR, XRD, and SEM-EDX analyses, while liquid extracted from PS was characterized by GC-MS analysis. Results revealed that moisture and volatile matter of PS decreased from 23.31 to 9.98 wt % and 65.10 to 62.71 wt %, respectively, while fixed carbon increased from 9.16 to 23.21 wt % after Soxhlet extraction. Thermogravimetric analysis (TGA) suggested four distinctive zones during the thermal decomposition of PS. Kinetic triplets (activation energy, frequency factor, order of reaction) for major devolatilization zone of organic compounds for raw and filtered PS was found to be 27.80 kJ/mol, 63.802 min^{-1}, 0.07 and 35.01, 272.91, 0.11, respectively. TGA indicated that sludge can be processed by pyrolysis in the temperature range of 250 to 650 ℃. Many value-added chemicals were identified in liquid extracted from OPS among which phytol (50.72 %) was the most abundant.

5.1 Introduction

The rapid increase in the global population has provided much impetus to major sources of energy supply, such as coal, petroleum, and natural gas. The inclination towards petroleum-derived fuel is constantly growing [167]. A huge amount of oily petroleum sludge (OPS) is produced during crude oil refining as point out in chapter 1. In the petroleum industry, OPS is generated by both upstream and downstream operations [168]. The major constituents of OPS are aliphatic and aromatic hydrocarbons containing nitrogen, sulfur, oxygen, and asphalt [169, 170]. OPS also contain toxic metals such as Pb, Cu, Cr, Cd, Ti, Ni, Co, As, and V [9, 171]. It also contains a complex mixture of contaminated soil or sediments, which constitute different chemical species with different physicochemical properties depending upon the source of generation [4, 5]. Due to its hazardous nature, the OPS have adverse impact on the environment. The insufficient treatment and the improper disposal of the OPS can cause immense problem to the environment, human health, aquatic life and the fertility of soil [21, 22].

In the past various methods have been employed for recycling, oil recovery, removal of toxic metals, and remediation of hazardous sludge as discussed in chapter 1. Moreover, complex physicochemical characteristics of OPS also affect the selection of processes for appropriate utilization and disposal. Among the various explored processes, thermochemical treatment of OPS has received significant attraction in recent years for efficient utilization of OPS. Therefore, the utilization of OPS for a generation of energy under thermochemical treatment process has attracted the various research society of the world. Also, the co-pyrolysis of biomass with petroleum sludge has attracted attention in recent years. The thermochemical process classification is discussed in chapter 1. The physicochemical characterization of feedstock, such as moisture content, volatile matter, chemical composition, kinetic parameters, and surface characteristics, plays a crucial role in the selection of appropriate thermochemical conversion techniques [63]. In the past, efforts have been made to study combustion [172, 173] and pyrolysis [11, 21, 172, 174] of OPS. However, an in-depth analysis of petroleum sludge has scarcely been reported. In addition, solvent extraction has been widely used for the recovery of oil from petroleum sludge; however, the effect of solvent extraction on physicochemical characteristics of petroleum sludge has been scarcely reported. Also, as per the author's knowledge, the effect of solvent extraction on kinetic triplet (activation energy, frequency factor, order of reaction) of petroleum sludge has not been reported.

Therefore, in the present chapter physicochemical characterization of OPS was investigated. The liquid was extracted from the sludge using Soxhlet method by selective non-polar solvents. The petroleum ether, hexane, toluene, and benzene were used as a solvent. Both the sludge (before and after extraction) extracted by hexane were characterized for proximate, ultimate, TGA/DTG/DTA, FTIR, XRD, and SEM-EDX analyses. The kinetic triplets (activation energy, frequency factor, order of reaction) were calculated using multiple regression analyses of TGA data. The liquid extracted from the sludge after Soxhlet extraction was analyzed through GC-MS analysis after the removal of a solvent to identify the chemical composition.

5.2 Material and methods

5.2.1. Material

The OPS used in this study was collected from the ETP of the petroleum refinery located in northern India. Wastewater from the various processing units, oil spills, and waste from the bottom of storage tanks are treated at the ETP of a refinery. The liquid effluent is discharged and the sludge from the bottom of clarifiers is sent to a sludge management unit where other treatment processes for sludge are carried out. The sample was placed in a cold room to preserve the originality of its characteristics. The different chemicals used in this study were of AR grade. In the present chapter original, OPS was coded as S1, and PS obtained after Soxhlet extraction was coded as S2.

5.2.2 Soxhlet extraction method

Soxhlet extraction was used to separate the liquid component of OPS by using the petroleum ether, hexane, toluene, and benzene as solvent separately. Before soxhlet extraction, the OPS was dried at 105 °C for 24 h to evaporate the water content in the sludge. Then, 10 g OPS was placed on a thimble (filter paper cut in the size of the thimble portion of Soxhlet apparatus), which was already filled with 50 ml of solvent, where the soluble components were slowly transferred to the solvent from the OPS. When the liquid overflow from thimble portion, the siphon aspirates it from thimble and transfers it to the distillation flask. The distillation flask temperature was set at a boiling temperature of the selected solvent (petroleum ether: 40 °C, hexane: 60 °C, toluene: 100 °C, benzene: 80 °C). The extractant collected in the distillation flask was re-circulated through the sample again and again until the solvent inside the siphon tube becomes colorless. The assembly of Soxhlet apparatus is considered a batch system. After this, the condensed portion was removed and the solution in the distillate flask was heated at boiling point of a solvent and the remaining liquid was collected. The liquid left after Soxhlet extraction of sludge in Soxhlet apparatus was analyzed by the GC-MS (Shimadzu QP-2010 Plus with Thermal Desorption System TD 20, Japan). Helium was used as a carrier gas. 1 μL of the sample was injected in the column (60.0 m × 250 μm) with a split ratio of 10:1, while the injector temperature was maintained at 280℃. The initial oven temperature was 60 ℃ for 2 min and then was increased up to 140 ℃ with a ramping rate of 5 ℃/min and holding time of 5 min. Again, the temperature was increased to 300 ℃ with a ramping rate of 5 ℃/min and held constant for 5 min. The OPS was collected from the ETP of a refinery, where the wastewater and solid sludge are separated. The oil and grease present in a waste coming to ETP was screamed or separated in clarifier of ETP i.e. the OPS significantly contains hydrocarbons. Oil and grease are immeasurably present in OPS.

5.2.3 Characterization of PS

The proximate analysis of the S1 and S2 was performed. The moisture content (MC), volatile matter (VM), and ash content (AC) was calculated by using the standard protocol of ASTM D3173, ASTM D3175, and ASTM D3174, respectively. The fixed carbon content was calculated by difference (100 − (MC + VM + AC)). A CHNS elemental analyzer (Euro vector EA element analyzer) was employed to determine the weight percent of carbon, hydrogen, nitrogen, and sulfur content of both S1 and S2. The bomb calorimeter (RSB3, Rajdhani Scientific inst. Co., India) was used to determine the high heating values (HHV) by using the standard method ASTM D5685-10A. SEM, EDX, and FTIR analysers were used as discussed in chapter 3. The spectrum was recorded in the wavenumbers ranging from 4000 to 400 cm^{-1}. The X-ray diffraction (XRD) was analyzed by powder pattern method [175] using an instrument (Ultima IV, Rigaku Corporation, Japan) for the identification of crystalline phases of sludge with a scanning rate of 5^{o} per min with a step size of 0.02° in the range of 0 to 80° (2θ). The pyrolysis of OPS was carried out in a TGA analyzer (EXSTAR TG/DTA 6300). The TGA was performed at a heating rate of 10 ℃/min from the ambient temperature to 900 ˚C. Approximately 10±0.05 mg of PS sample (as-received) was loaded in an alumina crucible and placed in the heating zone of TGA. A small amount of samples was taken to mitigate the temperature gradient and mass transfer limitations. The pyrolysis was performed in a nitrogen (99.999 % pure) environment with a flow rate of 100 mL/min to create an inert atmosphere and to ensure the prevention of secondary cracking of fuel gases. The TGA and DTG and DTA data were recorded for further analysis. Before every experiment empty run (without sample) was taken to determine the TG baseline for eliminating the buoyancy effect.

5.2.4 Estimation of kinetic parameters using thermogravimetric analysis

The kinetics for thermal degradation of sludge obtained after Soxhlet extraction was investigated using thermogravimetric analysis by employing the multiple regression method. This method allows the calculation of the kinetic triplets (activation energy, frequency factor, order of reaction) for the entire thermal degradation range at a single heating rate during TGA analysis. For the analysis of thermal degradation behavior and estimation of kinetic parameters, the whole temperature range was divided into four zones. The first zone (25-105℃) and the second zone (105-350℃) correspond to the removal of free and bound moisture along with release of light volatile matter, respectively, from the sludge. While, the third zone (305-520℃) and the fourth zone (520-900℃) corresponds to intense devolatilization and decomposition of inorganic matter, respectively, present in the sludge. The second and third zone was considered as the main pyrolysis region of sludge and kinetic triplets were calculated for the same due to significant weight loss in these two zones.

The general degradation equation can be written as:

$$-\frac{d\alpha}{dt} = \mathrm{K}\alpha^{n} \tag{1}$$

where α is the conversion, K is the rate constant, n is the order of reaction, and t is the time taken for a different level of conversion. The conversion α can be defined using Eq. (2).

$$\alpha = \frac{w_t - w_f}{w_o - w_f} \tag{2}$$

where w_o and w_f are the initial and final mass of a sample, respectively, while w_t is the mass of a sample at any time t.

K is the rate constant which is a function of temperature and can be correlated using Arrhenius expression given as follows:

$$K = A\, exp\left(\frac{-E}{RT}\right) \quad (3)$$

where A is the pre-exponential factor (min^{-1}), E is the activation energy of decomposition reaction (kJ/mol), R is the universal gas constant (kJ/mol. K), and T is the absolute temperature (K).

combining Eq. (1) and (3) gives the expression:

$$-\frac{d\alpha}{dt} = A\, exp\left(\frac{-E}{RT}\right) \alpha^n \quad (4)$$

Now, again combining Eq. (2) and (4) gives the expression

$$\frac{-1}{w_o - w_f}\frac{dw}{dt} = A\, exp\left(\frac{-E}{RT}\right)\left(\frac{w_t - w_f}{w_o - w_f}\right)^n \quad (5)$$

Integrating of Eq. (5) gives the expression:

$$\ln\left(\frac{-1}{w_o - w_f}\frac{dw}{dt}\right) = \ln(A) - \left(\frac{E}{RT}\right) + n\ln\left(\frac{w_t - w_f}{w_o - w_f}\right) \quad (6)$$

where, $\frac{dw}{dt}$ is the rate of change of mass of sludge sample. Now the Eq. (6) can be written in linear form as:

$$y = B + Cx + Dz \quad (7)$$

where $y = \ln\left(\frac{-1}{w_o - w_f}\frac{dw}{dt}\right)$; $x = \frac{1}{T}$; $Z = \ln\left(\frac{w_t - w_f}{w_o - w_f}\right)$; $B = \ln(A)$; $C = \frac{-E}{R}$; D = n

The value of *B*, C, and D can be calculated by using regression analysis in Microsoft Excel software. Then based on the value of *B*, C, and D, the frequency factor, activation energy, and order of reaction can be calculated.

5.3 Results and discussion

5.3.1 Soxhlet extraction analysis

Liquid present in OPS was extracted by using the Soxhlet apparatus by using petroleum ether, hexane, toluene, and benzene as solvents. The liquid present in OPS creates problems in the treatment of solid sludge as leachate conditions are observed during the handling of petroleum sludge for treatment process. Therefore, it is of prime importance to remove liquid from OPS. The 50 ml of solvent is used to extract the liquid from 10 g of OPS by different solvents separately. The amount of solvent does not need to vary because the Soxhlet apparatus runs in continuous mode. The number of an experimental run of liquid extracted from PS uploaded in distillation flask was stopped at a condition where clear solvent in siphon tube was observed. The results obtained from Soxhlet extraction experiment i.e. amount of solid and liquid separated from OPS are given in Table 5.1. Results showed that hexane can extract the maximum amount of liquid from the OPS followed by petroleum ether, toluene, and benzene. The affinity of hexane is greater towards the hydrocarbons having oily characteristics due to its non-polar nature [109]. Thus, the maximum liquid constitute of OPS was extracted by hexane. The OPS contains hazardous metal which easily removes by the solvent. In addition, the lesser amount of liquid present in the OPS will be beneficial for the thermochemical treatment since it can overcome the problem related to leaching conditions for handling toxic metal [176, 177]. Similar results were obtained by Zhu et al. [178], and Taiwo et al. [51] during solvent extraction of sludge using hexane. Hexane also favors low extraction temperature, which lowers the heating cost and prevents thermal degradation of sludge. Thus, it was found that hexane provides the better results as compared to other used solvents. Therefore, further analysis was carried out for OPS before and after solvent extraction using hexane.

Table 5. 1 Soxhlet extraction of OPS using different solvents.

Solvent	Amount of liquid extracted (g)	Amount of solid left (g)
Petroleum ether	2.2	7.8
Hexane	2.5	7.5
Benzene	1.7	8.3
Toluene	2.0	8.0

5.3.2 Physicochemical characteristics of OPS

5.3.2.1 Proximate, ultimate and calorific value of OPS

The PS was dark black in color and similar in appearance to the black soil. The calorific value, proximate, and ultimate analysis results of OPS samples before and after soxhlet extraction are presented in Table 5.2. The moisture content, volatile matter, fixed carbon, and ash content of sludge (S1) are found to be 23.31, 65.10, 9.16, and 2.43%, respectively. While, moisture content, volatile matter, fixed carbon, and ash content of sludge (S2) after liquid extracted were found to be 9.98, 62.71, 23.21, and 4.10%, respectively. The decrease in moisture content in sludge might be due to the ability of the solvent to dissociate the oil-water emulsification bond in the sludge during the filtration process. Thus, both free and flocculated water can be removed by the Soxhlet extraction process [21]. The higher HHV (18.30 MJ/kg) as compared to sludge S1 (12.42 MJ/kg) attributed to the lower moisture content in the sludge (S2). The higher moisture content of original sludge hindered its utilization in thermochemical processes. The volatile matter in sludge S1 and S2 was found to be 65.10, 62.71 wt%, respectively. The higher volatile matter of sludge makes it excellent feedstock for the pyrolysis process since it may give a higher yield of pyrolytic oil. The result of an ultimate analysis revealed that Soxhlet extraction has a significant effect on the carbon, hydrogen, oxygen, and nitrogen content of sludge. The carbon content of sludge S1 is 53.63 wt %, while for sludge S2 it is found to be to 58.31 wt %. The hydrogen and oxygen content decreased from 6.52 to 6.08 wt % and 34.93 to 29.69 wt %, respectively, once the sludge is treated through Soxhlet extraction. In addition, marginal densification of nitrogen and sulfur content in sludge was also noticed after Soxhlet extraction.

Table 5. 2 Proximate and ultimate analysis of petroleum sludge

Properties	Sludge S1	Sludge S2
Proximate analysis		
Moisture content (wt %)	23.31	9.98
Volatile matter (wt %)	65.10	62.71
Fixed carbon (wt %)	9.16	23.21
Ash content (wt %)	2.43	4.10
Ultimate analysis		
C (wt %)	53.63	58.31
H (wt %)	6.52	6.08
N (wt %)	1.76	2.69
O (wt %)	34.93	29.69
S (wt %)	3.16	3.23
HHV (MJ/kg)	12.42	18.3

5.3.2.2 Thermogravimetric analysis of OPS and estimation of kinetic parameters

The thermogravimetric analysis of OPS (S2) obtained after Soxhlet extraction was performed to investigate the thermal decomposition behavior of sludge. Fig. 5.1(a), (b), and (c) represent the TGA, DTG, and DTA analysis of sludge S1 and S2, respectively. It is seen that within the temperature range of ambient to about 900 ℃, the weight loss with temperature profile can be divided into four distinct zones. In the Ist zone (25-105 °C), there is a slow decrease in the mass of OPS with a weight loss of 6.02 %, due to loss of surface moisture. In the IInd zone (105-350 °C), 30.01 % weight loss was observed due to the removal of bound moisture and formation and vaporization of some low boiling components from sludge [21]. In the IIIrd zone (350 to 520 °C), there is a fast and steady decrease in the mass of

OPS by 31.32 % can be attributed to the decomposition of a major portion of sludge constituents that are primarily organic in nature [21].

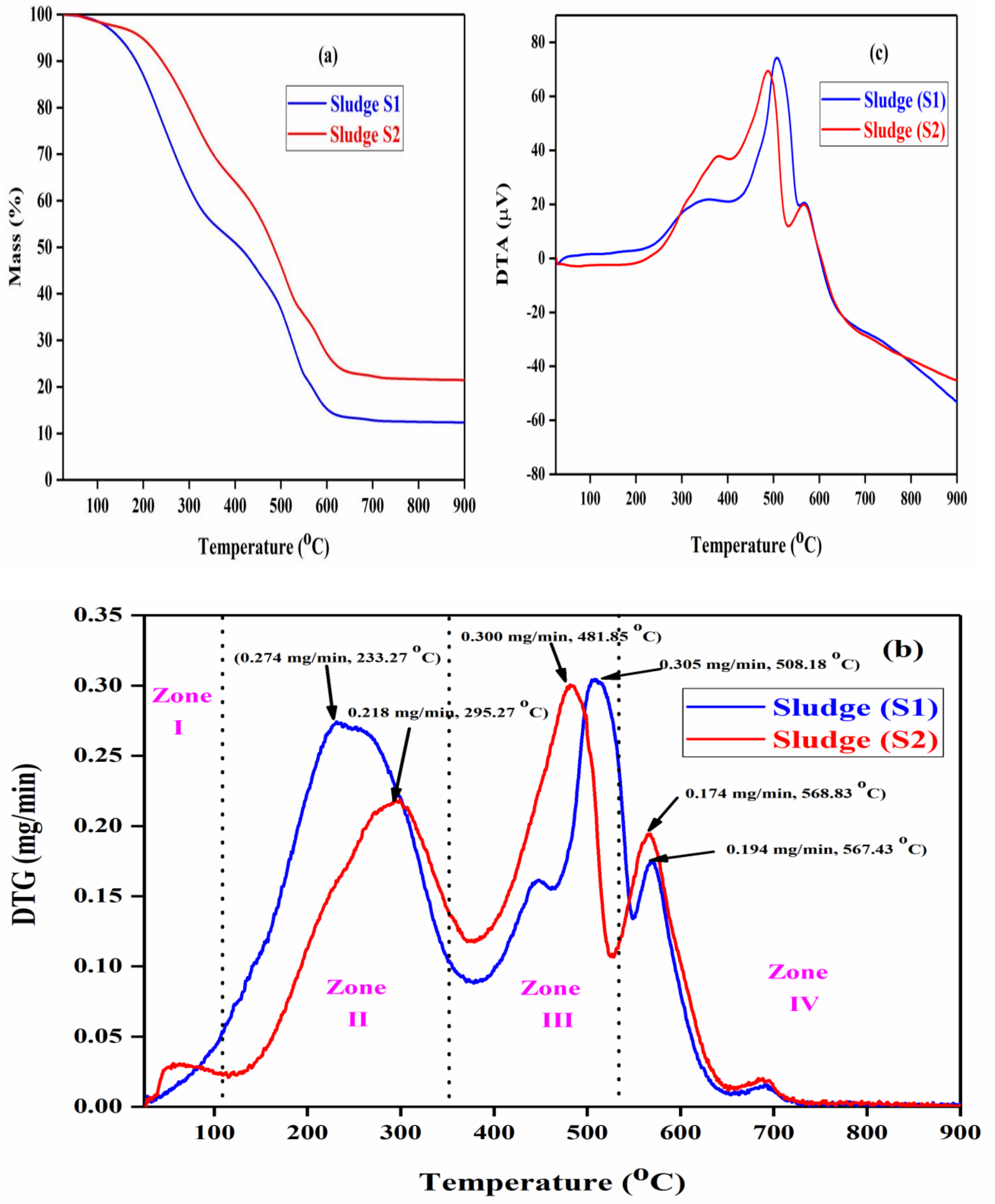

Figure 5. 1 (a) TGA (b) DTG (C) DTA analysis of sludge S1 and S2 obtained after Soxhlet extraction.

The first peak in a DTG curve corresponds to the decomposition of organic matter associated with sludge, while the second and third peaks might correspond to the decomposition of inorganic matter such as carbohydrates and clay [179]. In the Zone (520-900 ℃), the rate of decrease in mass of the residual sludge sample once again becomes slow up to 900 ℃. This region is characterized by the conversion of high boiling point organics to char. Meanwhile, DTA analysis revealed that thermal decomposition of sludge is characterized by both endothermic and exothermic processes (Fig. 5.1 (c)). Three endothermic peaks are observed between temperature ranges of 250-378, 378-489, and 500-565℃, while three exothermic peaks are observed in a temperature range of 489-500, 565-650, and 650-900℃.

Based on the thermogravimetric analysis data, the kinetic triplet (activation energy, frequency factor, order of reaction) for second and third zones was calculated and the results were given in Table 5.3. The activation energy, frequency factor, and order of reaction for sludge S1 in the second zone were found to be 20.97 kJ/mol, 105.022 min^{-1}, and 0.46, respectively, and for the third zone, it was found to be 27.83 kJ/mol, 63.803 min^{-1}, and 0.07, respectively. The kinetic triplet for sludge S2 in the second zone was found to be 28.58 kJ/mol, 496.084 min^{-1}, and 0.37, respectively, and for the third zone, it was found to be 35.01 kJ/mol, 272.914 min^{-1}, and 0.11, respectively. The lower value of activation energy for second zone than the third zone may be attributed to the energy required for vaporization of bound moisture and lighter volatiles from the sludge in second zone, while for third zone, energy is required for chemical decomposition [21]. Also, the increase in activation energy in the case of sludge S2 might be due to lower volatile matter. The lower activation energy along with high volatile matter in the sludge makes it suitable feedstock for pyrolysis process.

Table 5. 3 Kinetic parameters for the main pyrolysis zone of petroleum sludge.

Zone	Significance	Activation energy (kJ/mol)		Frequency factor (min^{-1})		Order of reaction	
		SludgeS1	SludgeS2	Sludge S1	Sludge S2	SludgeS1	SludgeS2
2nd zone	Removal of bound moisture and light volatile matter	20.97	28.58	105.022	496.084	0.46	0.37
3rd zone	Intense devolatilization	27.83	35.01	63.802	272.914	0.07	0.11

5.3.2.3 FTIR analysis of OPS

The FTIR analysis was carried out to identify the functional groups associated with sludge (S1 and S2). The FTIR spectra are shown in Fig. 5.2. It can be observed that both the sludge shows a similar pattern of peaks. However, the transmittance intensity of peaks is higher in case of S1 as compared to S2. The sludge S2 was obtained after Soxhlet extraction of sludge S1. The viscous liquid component of sludge S1 was separated through Soxhlet extraction. This might be the reason for smaller intensity in case of S2 because various chemical compounds were separated from S1 through Soxhlet extraction. The peaks in OPS were identified in the wavenumber range of 3400-3209 cm^{-1}, 3016-2706 cm^{-1}, 1750-1511 cm^{-1}, 1500-1272 cm^{-1}, 1250-900 cm^{-1}, 802-470.5 cm^{-1}, while, the major peaks were detected at 2939 cm^{-1}, 1434 cm^{-1}, and 1049 cm^{-1}. Table 5.4 represents the summary of FTIR absorption bands of the functional group present in OPS. The waveband 3400–3209 cm^{-1} was attributed to hydroxyl groups; the peak between 3016-2706 was attributed to the presence of $–CH_2$ functional group. The band between 1750-1511 corresponds to aromatic rings; peaks at 1434 in-between bands 1500-1270 was attributed to the presence of methyl ($-CH_3$) and methylene

($=CH_2$); peak 1049 due to C-OH stretching. Waveband observed in the regions of 900-630 cm^{-1} was attributed to aromatic carbon-carbon rocking vibrations.

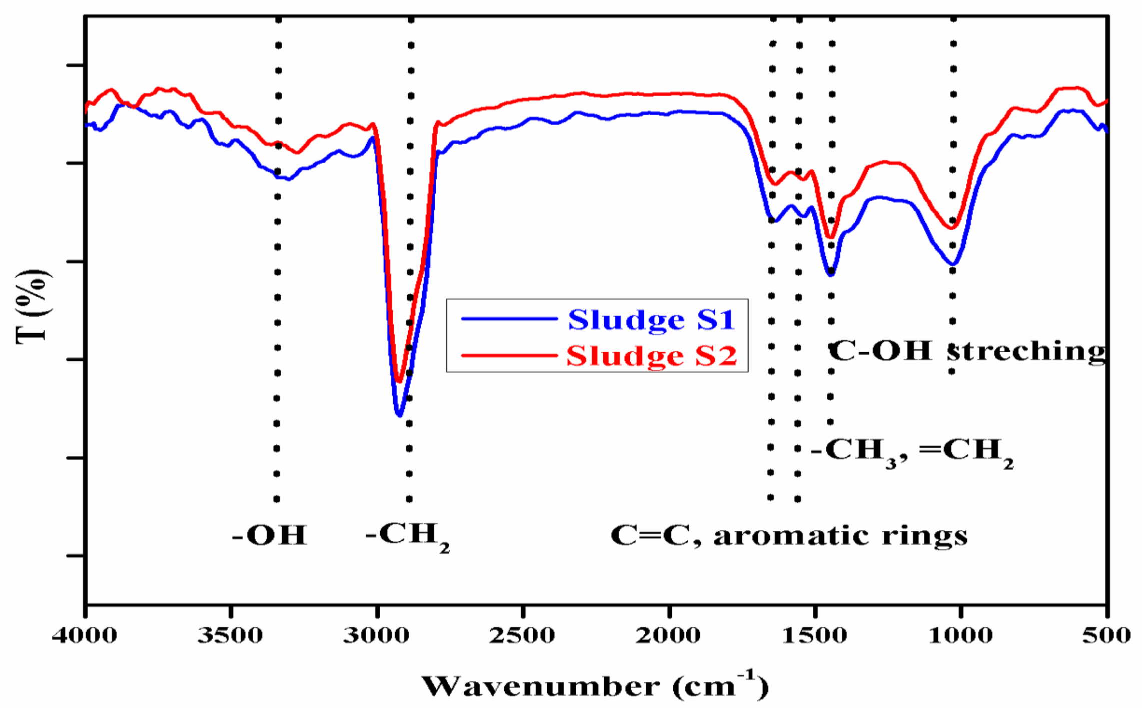

Figure 5. 2 FTIR analysis of original sludge (S1) and sludge after Soxhlet extraction (S2)

Table 5. 4 Summary of FTIR absorption bands of the functional group present in petroleum sludge

Band position, cm^{-1}	**Functional group**
3400- 3209	-OH
3016-2706	$-CH_2$
1750-1511	C=C, Aromatic rings
1500-1270	$-CH_3$, $=CH_2$
1250-870	C-OH stretching
900-630	Aromatic carbon-carbon rocking vibration

5.3.2.4 SEM-EDX analysis of OPS

The morphology of original sludge (S1) and sludge obtained after Soxhlet extraction method (S2) was studied using SEM-EDX analysis. The SEM-EDX image, along with color mapping, is depicted in Fig. 5.3 (a) and (b). It can be observed that the sludge (S2) has irregular flakes with a spherical ball-like structure [180], while the oily and shiny surface can be seen in case of sludge (S1). Also, the sludge (S2) has a fractured structure with a large number of open-pore and voids microstructure. However, the structure of sludge became clumsy due to the agglomeration of sludge particle during Soxhlet extraction. The pores are also visible on the surface of sludge (S2) with a strong linkage between the pores. The strong and porous structure of sludge is favorable for an adsorption process. Table 5.5 represents the EDX analyses of sludge S1 and S2. Various elements such as carbon (C), oxygen (O), nitrogen (N), potassium (K), sulphur (S), magnesium (Mg), etc., were identified on the surface of sludge (S1). Meanwhile, after Soxhlet extraction, a sharp decrease in carbon and oxygen content along with the densification of some elements such as potassium, magnesium, cobalt, etc., was observed in case of sludge (S2). The densification of these elements on the surface of sludge (S2) may facilitate its thermochemical conversion by acting as a catalyst.

Table 5. 5 EDX analysis and color image of elements present on petroleum sludge.

Element	Element percentage		Color	Element	Element percentage		Color
	Sludge S1	Sludge S2			Sludge S1	Sludge S2	
Carbon	60.35	73.44		Silver	0.33	0.35	
Nitrogen	1.22	0.89		Potassium	0.89	1.23	
Oxygen	10.48	5.45		vanadium	0.53	0.40	
Sodium	0.77	0.89		Chromium	0.78	0.42	
Magnesium	0.59	0.40		Manganese	0.28	0.63	
Aluminum	1.79	1.08		Iron	1.38	2.95	
Phosphorus	1.30	0.30		Cobalt	1.25	1.55	
Sulphur	6.78	4.86		Nickel	0.65	0.69	
Lead	7.29	6.20		Cupper	0.44	0.38	
Argon	0.01	0.01		Zinc	0.46	0.34	

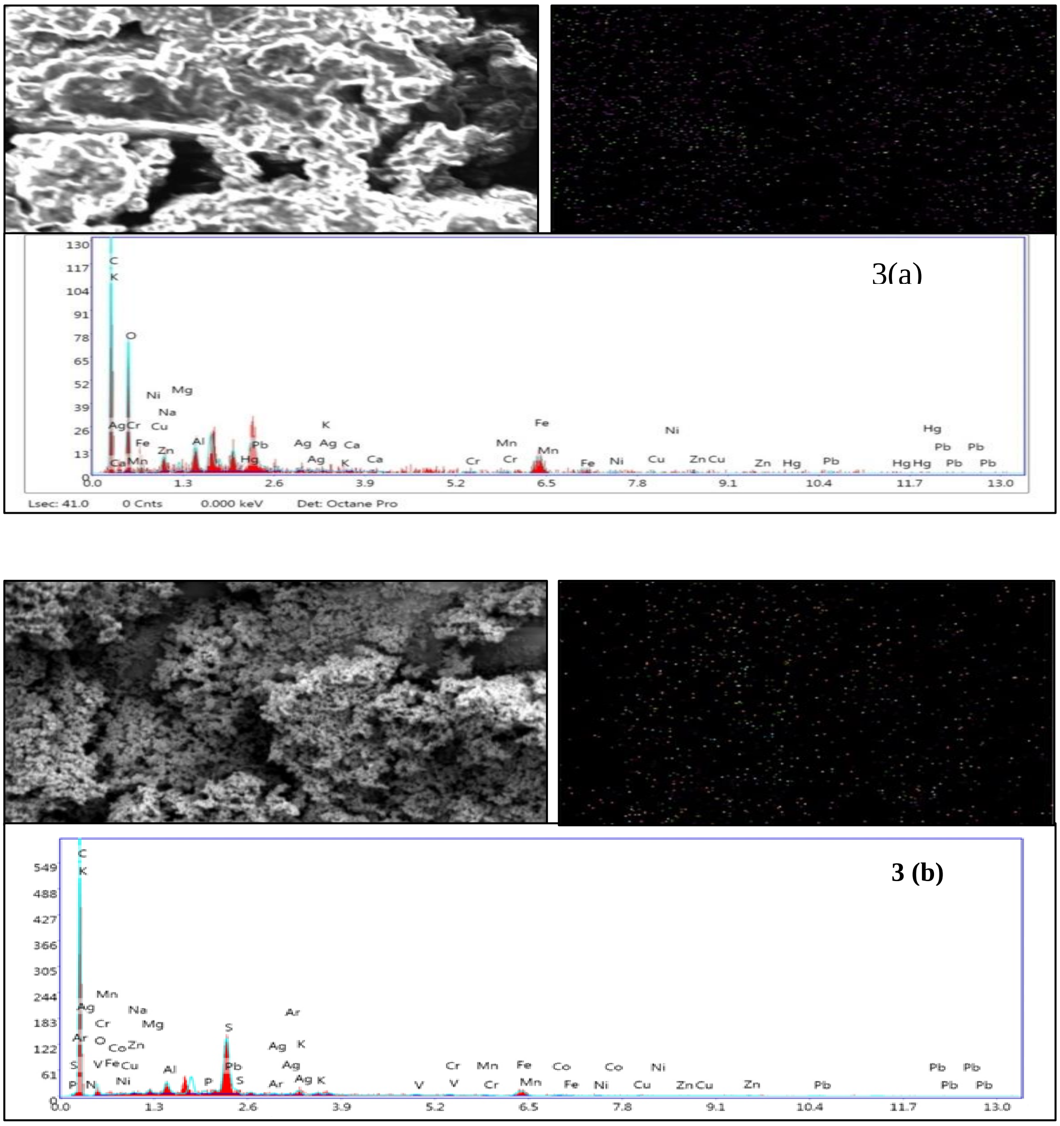

Figure 5. 3 SEM-EDX analysis and color mapping of sludge (a) OPS sludge (S1), (b) OPS Soxhlet extraction (S2)

5.3.2.5 XRD analysis of OPS

The XRD analysis of original sludge (S1) and sludge separated by Soxhlet extraction (S2) was performed to investigate the composition qualitatively as shown in Fig 5.4. For both the sludge, two sharp characteristic peaks are identified at 2θ = 26.74°, and 29.55°. The first peak corresponds to calcium carbonate, while, the second peak corresponds to silica oxide [181]. Gong et al. [182] concluded that sludge mainly contains silicon, aluminum, and calcium. Wang et al. [183], illustrated that presence of these peaks is also attributed to the crystalline structure of carbonaceous material present in sludge. The (002) plane corresponds to standard graphite material, while the (100) plane is associated with diffraction of graphite layer [183, 184]. The peaks related to heavy metal present in the sludge are not identified due to their small amount. Meanwhile, the intensity of peaks is higher in case of sludge (S1) as compared to sludge (S2). This might be a result of the removal of oil fraction from sludge S1. Thus, sludge S1 has a more irregular carbon structure after Soxhlet extraction [183, 185]. Thus, the crystallinity of sludge decreased after Soxhlet extraction.

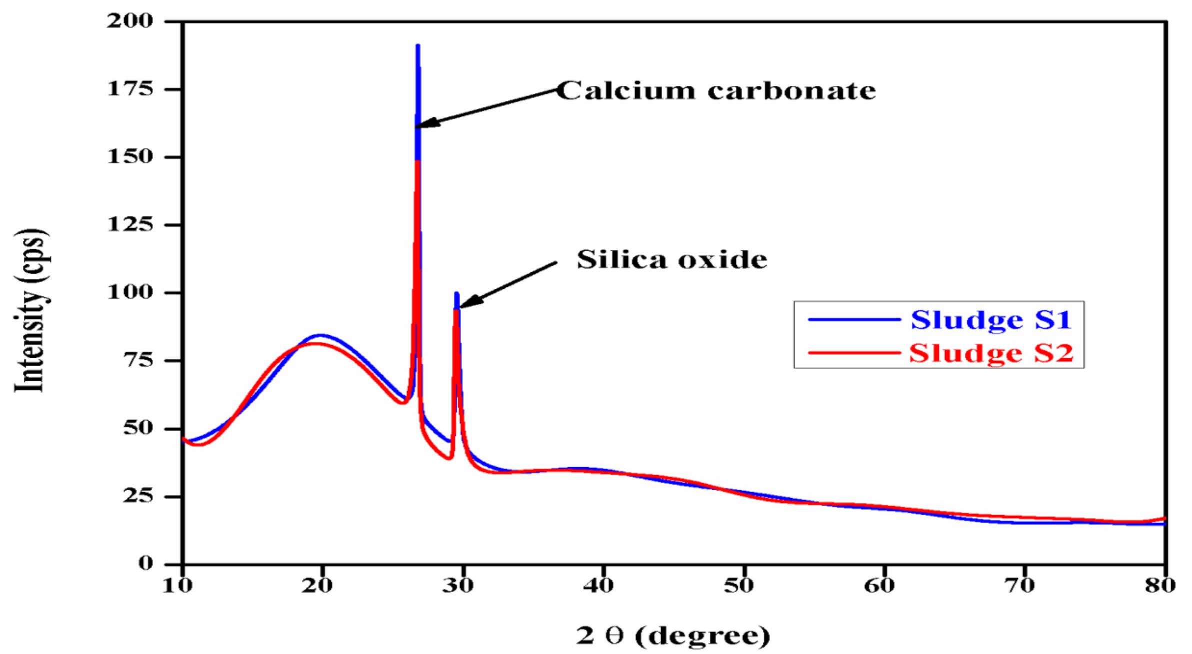

Figure 5. 4 XRD analysis of original sludge (S1) and sludge after Soxhlet extraction (S2)

5.3.3 Characteristics of liquid extracted using Soxhlet extraction

5.3.3.1 Physical properties and chemical composition of liquid from sludge after Soxhlet extraction

The liquid obtained after Soxhlet extraction was characterized for its physical properties such as higher heating value (HHV), viscosity, pH, and density. The chemical composition of liquid was investigated using GC-MS analysis. The liquid obtained after Soxhlet extraction was highly basic in nature, having a pH of 8.5. The density and viscosity of liquid was 1.115 kg/m^3, and 1.09 mPa.s, respectively. The HHV of liquid was 10.74 MJ/kg. The GC-MS analysis was employed to identify the various chemical compounds present in the liquid extracted from sludge. The list of compounds identified from GC-MS analysis is presented in Table 5.5, and the GC-MS spectrum of liquid is shown in Fig. 5. 6. The compounds are identified by comparing the peaks with NIST database. Also, the compounds are quantified based on the percentage area under GC-MS chromatogram. The liquid fraction has compounds with carbon ranging from C8 to C24. The most abundant class of compounds present in liquid is aromatic (52.84 %) followed by alkanes (39.35 %) (Straight and branched-chain alkanes), acids (5.72 %), and alcohol (2.09 %), respectively. The major aliphatic hydrocarbon present in liquid is tridecane, N-cetane, 2-methyl decane, pentadecane, etc. while the most abundant aromatic compound is phytol (50.72 %). Phytol (IUPAC name, (2E, 7R, 11R)-3,7,11, 15-tetramethyl-2-hexadecen-1-ol) is acyclic diterpene alcohol that can be used as a precursor for the manufacturing of synthetic forms of vitamin E and vitamin K1. The oxygen-containing compounds such as acids and alcohol are present in a lesser amount which increases the stability of a separated liquid.

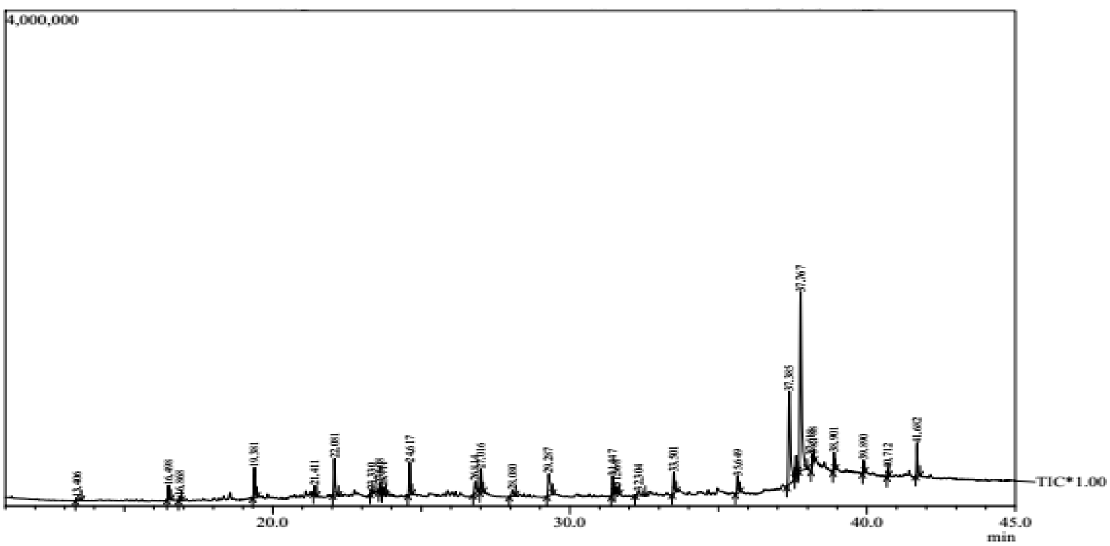

Figure 5. 5 GC-MS spectra of liquid extracted from sludge using a Soxhlet extraction method

Table 5. 6 GC-MS analysis of liquid extracted from petroleum sludge.

Peak	Compound Name	Molecular Formula	RT (min)	Area (%)
1	Oxalic Acid, Isobutyl Pentyl Ester	$C_{11}H_{20}O_4$	13.40	0.38
2	Tridecane	$C_{13}H_{28}$	16.49	1.64
3	4-Methylnonane	$C_{10}H_{22}$	16.86	0.46
4	Tridecane	$C_{13}H_{28}$	19.38	3.57
5	4,6-Dimethyldodecane	$C_{14}H_{30}$	21.41	0.87
6	N-Cetane	$C_{16}H_{34}$	22.08	4.99
7	1-Octadecanol	$C_{18}H_{38}O$	23.33	0.46
8	2-Methyldecane	$C_{11}H_{24}$	23.60	0.78
9	Oxalic Acid	$C_{21}H_{38}O_4$	23.71	0.77
10	Pentadecane	$C_{15}H_{32}$	24.61	4.12
11	2,4-Imidazolidinedione	$C_8H_6N_4O_5$	26.81	2.10
12	N-Cetane	$C_{16}H_{34}$	27.01	2.83
13	2,6-Dimethylundecane	$C_{13}H_{28}$	28.08	1.10
14	Heneicosane	$C_{21}H_{44}$	29.28	4.69
15	2,6,10,15-Tetramethylheptadecane	$C_{21}H_{44}$	31.44	2.33
16	3,7-Dimethyldecane	$C_{12}H_{26}$	31.56	1.12
17	Carbonic Acid	H_2CO_3	32.30	1.27
18	N-Octadecane	$C_{18}H_{38}$	33.50	2.70
19	2,6,10,15-Tetramethylheptadecane	$C_{21}H_{44}$	35.64	2.80
20	6,10,15-Tetramethylheptadecane	$C_{21}H_{44}$	37.61	1.96
21	Phytol Isomer	$C_{20}H_{40}O$	37.76	50.72
22	13-Octadecadienol	$C_{19}H_{36}O$	38.18	1.63
23	8-Heptylpentadecane	$C_{22}H_{46}$	38.90	1.68
24	8-Methyldecane	$C_{22}H_{46}$	39.89	1.12
25	2-Bromotetradecane	$C_{14}H_{29}Br$	40.71	0.59
26	1,2-Benzenedicarboxylic Acid, Dioctyl Ester	$C_{24}H_{38}O_4$	41.68	3.30

5.4 Conclusions

In this present chapter, physicochemical characteristics of petroleum sludge before and after Soxhlet extraction by using petroleum ether, hexane, toluene, and benzene as solvent was investigated. The main focus was given to examine the characteristics of petroleum sludge for its remediation using thermochemical conversion processes. It was found that among the used solvent hexane can extract the maximum amount of liquid from OPS. Further, the results revealed that moisture and volatile matter of sludge after Soxhlet extraction decreased by 60.5 and 3.67 %, respectively, while, fixed carbon content increased by 1.5 times the original sludge. The higher volatile matter of sludge favors its utility in the pyrolysis process since it may increase the yield of pyrolytic oil. The TGA/DTG analysis indicated that sludge can be processed in the temperature range of 250 to 650 ℃ during pyrolysis. Four distinct zones were observed during a thermal degradation of sludge. The second (105-350 ℃) and third (350 to 520 ℃) zones were related to the devolatilization of organic compounds from the sludge. Also, the kinetic triplet of sludge (S1) and (S2) for intense devolatilization zone was found to be 27.83 kJ/mol, 63.802 min^{-1}, 0.07, and 35.01 kJ/mol, 272.9146 min^{-1}, 0.11, respectively. XRD analysis showed that the crystallinity of sludge decreased after Soxhlet extraction due to a presence of some amorphous carbon. The densification of elements like potassium, magnesium, cobalt, etc., on the surface of sludge (S2), may favor its utility in thermochemical conversion processes by acting as a catalyst. The GC-MS analysis showed that the most abundant class of compounds present in liquid is aromatic (52.84 %) followed by alkanes (39.35 %) (Straight and branched-chain alkanes), acids (5.72 %), and alcohol (2.09 %), respectively. Overall, it may be concluded that the Soxhlet extraction process of petroleum sludge collected from the effluent treatment plant can enhance the physicochemical properties of sludge by reducing the moisture content and increasing the fixed carbon content at a cost of a slight decrease in a volatile matter for better utilization and remediation.

Based on the results of the present chapter thermochemical conversion techniques can be a possible route for remediation of hazardous petroleum sludge. Meanwhile, among the various thermochemical techniques pyrolysis might be the most efficient process because of higher volatile matter, lower moisture, and activation energy of petroleum sludge. Pyrolysis has also gained dominance over other conversion techniques because the main product from pyrolysis is pyrolytic oil which can reduce the extra pressure over conventional fuels such as petroleum and diesel etc.