Modelling an End-of-Pipe Technology for Processing Petroleum Oily Sludge

ABSTRACT

An end-of-pipe technology for processing oily sludge using hydrocyclone is modelled in this study and then compared with an end-of-pipe using centrifugation with a science filter treatment system. The end-of-pipe technology design is proposed based on the characterization of physical and chemical data of oily sludge obtained from a national refinery in Port Harcourt, Nigeria. The aliphatic and aromatic hydrocarbons in the sludge, its metallic components and water content were characterised using gas chromatography. The ChemCad software is used for computer model simulation basis and computer simulation stream flow of the end-of-pipe system (hydrocyclone and compartment separator). The results show that the solids in the underflow from the cyclone contain about 3.8% by mass hydrocarbons and 4.06% water by mass. The hydrocarbon content of the hydrocyclone overhead recovered via the component separator bottoms contains 97.9%, 1.5% and 0.9% masses of hydrocarbon, water and solids respectively. The Chem Cad software is used to process data obtained from laboratory results to simulate design of stream flows. The end-of-pipe (centrifugation) filter technologies for sludge treatment is designed for 75% optimal oil recovery with zero solids and water content in the recovered oil making it high quality product largely due to the filtration system unit incorporated. The high oil recovery of 97.9% with a low carbon foot print in our proposed end-of-pipe technology model may be attributed to the use of natural hydrocarbon solvent (kerosene) to process the sludge in a hydrocyclone and separation compartment which aided the extraction and oil recovery.

Keywords: Hydrocyclone, centrifugation, oil recovery, gas chromatograph, ChemCad software

Introduction

Petroleum extraction and refining are connected with many engineering and environmental problems. The accumulation of oily sludge in tanks is one of such problems. Disposal and treatment of sludge waste streams present a major challenge for refinery operators [1–4]. Several technologies exist for the disposal of sludge in tanks and saver pits of refinery petroleum products production [3, 5]. Green technology is a continuously evolving method to reverse environmental pollution from process systems [6, 7]. The existing technologies for sludge treatment are based on one or a combination of the following conventional methods: physical, chemical and thermal methods [8]. Physical methods include centrifuging, storage, landfilling, lime stabilization, stabilization and solidification and are temporary solutions [3, 9–16]. Chemical methods (such as extraction, oxidative thermal treatment, treatment with fly-ash, solvent extraction, and pyrolysis) could lead to denaturing the sludge oil products [3, 9, 10, 16–18]. Thermal treatment (such as desorption, combustion and incineration) could permanently impair sludge to the end that products from sludge treatment are not easily reusable. This alternative technology solution has been reported that optimizes sludge processing and treatments have not been found to be optimal. The biological methods include land farming, bio-reactor treatment and composting [3, 9, 19–21]. All these methods can be classified as oil recovery methods, and sludge disposal methods [5], which are depicted in Fig. 1.

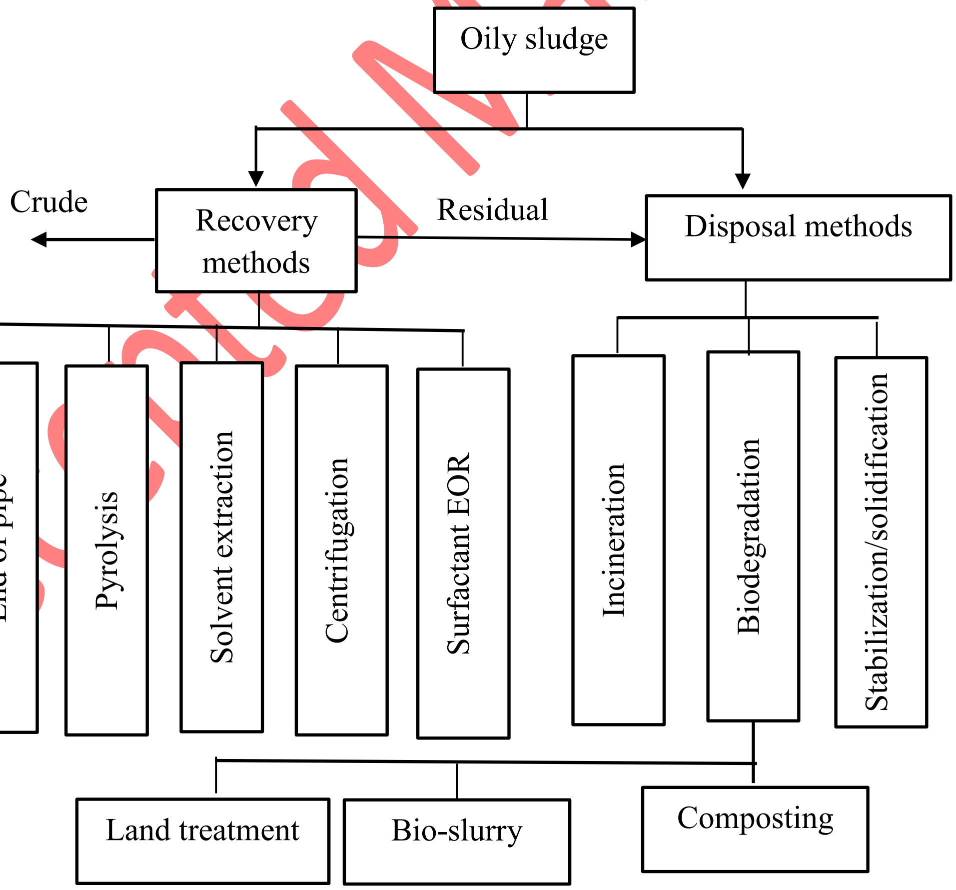


Fig. 1. Oil recovery methods, and sludge disposal methods [5]

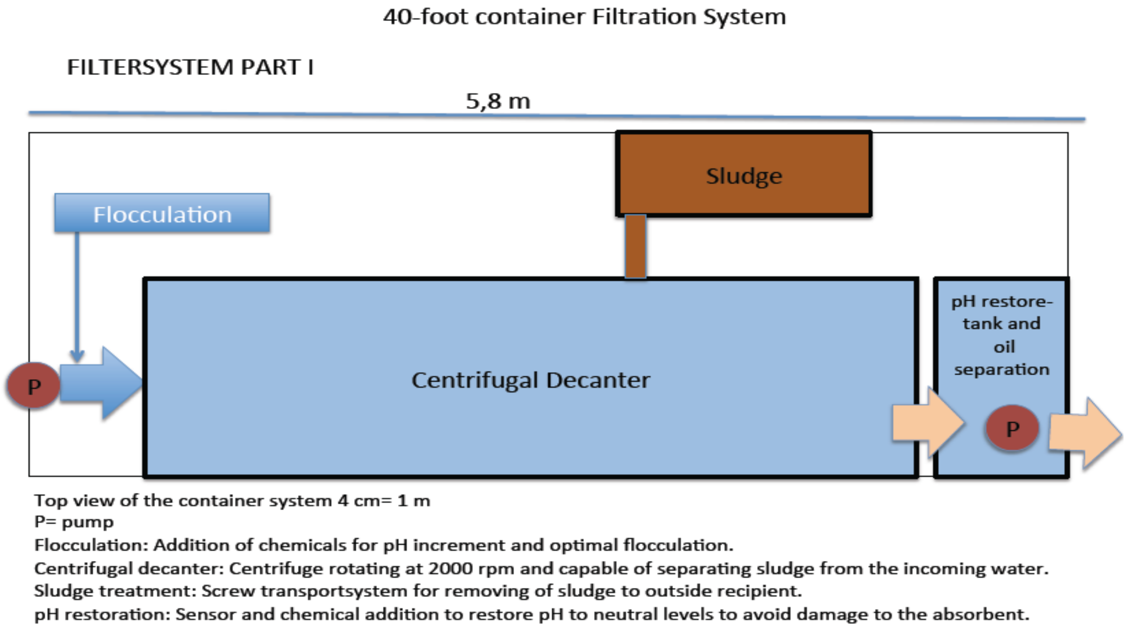
Therefore, the end-of-pipe technology solution scheme, proposed in this study, uses hydrocyclone and compartment separator that receives sludge mixed with kerosene, which is pretreated based on extensive data selection pre-trial studies, sludge data characterisation and model applications to design an applicable end-of-pipe technology for processing and treatment of oily sludge from a crude oil tank from refinery processes. The performance and model results of our proposed end-of-pipe technology solution scheme was compared with the end-of-pipe technology by centrifugation and filtration system as designed and developed by a company in Sweden (Scandinavian Green Export AB). The multifaceted end-of-pipe solution for sludge treatment approach recorded is derived from the characterisation of oily sludge samples with scientific measuring and analytical equipment at the University of Lagos Central Research Laboratory using gas chromatography, atomic absorption spectrometer and rheometer. Another milestone recorded in this investigation is the simulation using ChemCad software to design the end-of-pipe equipment specifications based on field work collated and measured data. The end result is the design of a hybrid solution for the end-of-pipe technology for tank cleaning, oily sludge handling with inputs to scientific observations. Therefore, the unmanned flexible end-of-pipe solution could provide oily sludge treatment that optimises recovery and cost up to 97%. Moreover, it ensures maximum return on environment and personnel safety. Most oily sludge in the petroleum industry is generated during crude oil exploration, production, transportation, and storage and refining processes [22, 23]. The compositions of the various amounts of the sludge generated from these processes are not the same but they contain a high concentration of petroleum hydrocarbons (PHCs) ranging from 5% to 86.2% by mass, and solid particles 5–46%, of which heavy metals are usually within the ranges of 7–80 mg/kg for zinc (Zn), 0.001–0.12 mg/kg for lead (Pb), 32–120 mg/kg for copper (Cu), 17–25 mg/kg for nickel (Ni), 27–80 mg/kg for chromium(Cr) and water in the range of 30–85% [4]. The concentration by mass of nitrogen, sulphur and oxygen in oily sludge is usually less than 3%, 0.3–10% and 4.8% respectively. The hydrocarbon phase of the sludge is fluidized by injecting petroleum cuts such as kerosene, naphtha, or diesel cuts, compatible with the sludge to be cleaned. However, the petroleum fractions naphtha and kerosene cuts are preferred for the process of hydrocarbon recovery in sludge treatment, reaching 83.99% using 7 mL only, while kerosene cut gives a higher hydrocarbon recovery of 97.2% using a sludge-solvent ratio of 1:4 (sludge in gram:solvent in mL These conditions are for the sludge for separation in the hydrocyclone by reducing the viscosity of the sludge and breaking the emulsion. This technology ensures close to 97% hydrocarbon recovery from crude oil sludge [24]. Sludge fluidization is determined by the chemical action of the heated kerosene cut, and by the mechanical action of jet washers that are installed on the tank roof.

Description of the End-of-Pipe System by centrifugation – Science Filtration System

The end-of-pipe system by centrifugation – Science Filter System (SFS), as developed by Scandinavian Green Export (SGE) AB in Goteborg, Sweden, whose contribution is by providing the design and field data for this research work, relies on the performance of the science absorber material and its properties. The science absorber material is at present a heat-treated pit material, which is hydrophobic and therefore, it is capable of absorbing oil and oil contaminated water. It can also work as an ion exchange and thus, it is capable of binding ionised metals in solution. This property can lead to a reduced leakage of unwanted soluble metal ions without any previous treatment. The metal-catching ability of the system is further increased by the addition of flocculating and pH increasing agents. Flocculation makes unwanted metals to precipitate as hydroxides. The floc can be sequestered by sedimentation (required tank reservoirs), filtration through bag filters (requires continuous changes) or band filters. The use of sand filters with backwashing abilities is also an alternative that helps in the water cleaning. To further decrease the impact of offensive material leaking into the environment, the system is equipped with active carbon filter whose amount depends on the load. The carbon will bind organic particles. An oxidation system (ozone or ultra-violet/TiO_2 based) may also help to decrease the organic load (i.e., chemical oxygen demand, COD) particles in the water.

End-of-Pipe SFS Pre-treatment System

Fig. 2 shows an end-of-pipe SFS pretreatment system design as developed by Scandinavian Green Export (SGE). To avoid risk of explosion, an inert gas, typically nitrogen, is injected into the tank before the cleaning process is started to reduce the oxygen level to below 8%. This level is maintained throughout the entire tank cleaning process. The hydrocarbon phase of the sludge is fluidized by injecting petroleum cut of kerosene stream, which is compatible with the sludge to be cleaned, through nozzles of jet washers at a pressure of approximately 6 bars in order to break, dissolve and disperse the sludge since kerosene cut gives a higher hydrocarbon recovery of 97.2% using a sludge-solvent ratio of 1:4 (i.e., sludge in gram: solvent in mL). This condition aids sludge separation in the hydrocyclone by reducing the viscosity of the sludge and breaking the emulsion. This technology ensures close to 100% hydrocarbon recovery from crude oil sludge [23]. Generally, jet washers are assembled in the centre of some roof supports to avoid the need to cut through the roof. Sludge fluidization is determined by the chemical action of the heated kerosene cut, and by the mechanical action of jet washers that are installed on the tank roof.



Top view of the container system 4 cm= 1 m
P= pump
Flocculation: Addition of chemicals for pH increment and optimal flocculation.
Centrifugal decanter: Centrifuge rotating at 2000 rpm and capable of separating sludge from the incoming water.
Sludge treatment: Screw transportsystem for removing of sludge to outside recipient.
pH restoration: Sensor and chemical addition to restore pH to neutral levels to avoid damage to the absorbent.

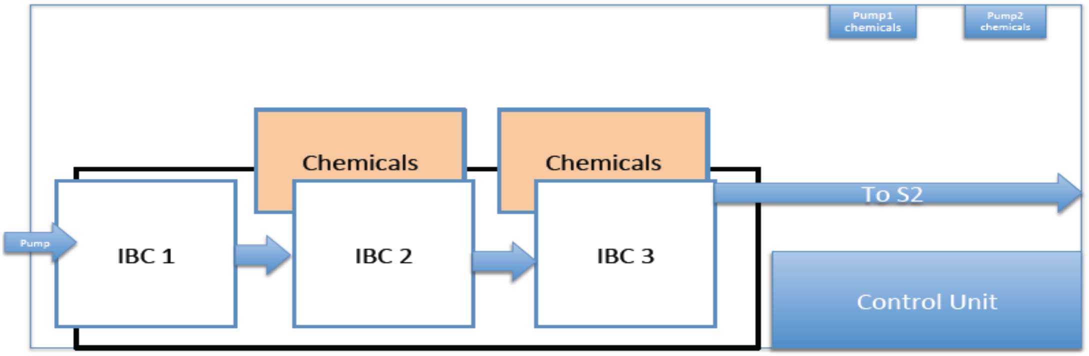
Fig. 2. End-of-pipe SFS pretreatment system

End-of Pipe SFS Desludging System

Fig. 3 shows an end-of-pipe SFS desludging system reproduced from Scandinavian Green Export. It is the first process of tank cleaning and it is also where most of the oily sludge from the tank is removed. The fluidized sludge is flushed out of the tank by the use of a suction pump. This pump is used to suction oil from the tank being cleaned. It then passes through heat exchangers to raise the temperature of the sludge-kerosene mixture to about 70°C in order to enhance oil separation and improve flow of the sludge [25–27]. The oil is pumped on to the recirculation module through hydrocyclones to separate heavy solid particles from the liquids. The oil from the bottom of the hydrocyclones matches the tank owner's specifications pumped directly to the pipeline. Further treatment is carried out in the separation module, comprising a decanter and an oil/water separator.

FILTER SYSTEM ÖCKERÖ

Filtration System Section S1



IBC1-IBC3 Sedimentation tanks (1m³ each)
Chemicals: Reservoirs for chemicals
Pump1 and 2 for chemicals: Pumps for chemical transport to flocculation and pH balance.
Control Unit: PLC (general) controller, pH controller, pump controllers, detection system controllers.

Fig. 3. End-of-pipe SFS desludging system

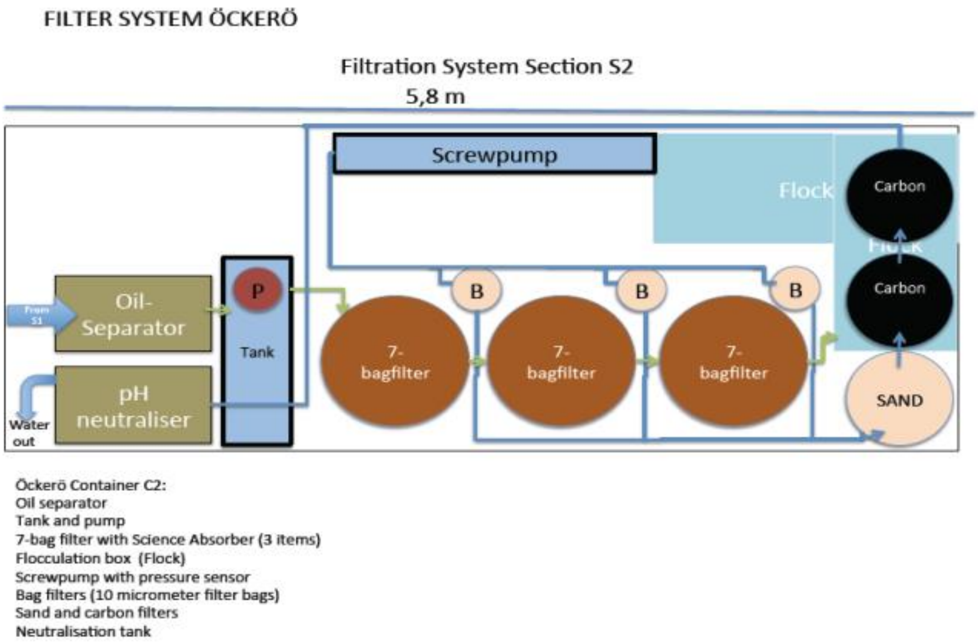
End of Pipe SFS Separation System I

Fig. 4 shows the end-of-pipe SFS separation system I reproduced from Scandinavian Green Export (SGE) while Fig. 5 depicts end-of-pipe SFS separation system II reproduced from SGE. Separation of the sludge takes place simultaneously with desludging and is separated into clean oil, solids and water [25]. There are two steps in the separation module. First, a liquid/solid separation takes place in the decanter, where solids are removed from the oil. The solids are deposited in containers for disposal or treatment, if required. If the recovered oil still contained water, a further oil/water separation is performed via the high-speed separator. The clean oil is pumped to the pipeline while the water can be pumped directly to a local wastewater treatment facility. Heat exchangers are used to facilitate the separation process. Regular laboratory tests ensure the separated oil conforms to the tank owner's specifications. The oil/water separator tank is also used to separate oil from water during water-washing operation.

Efficiency

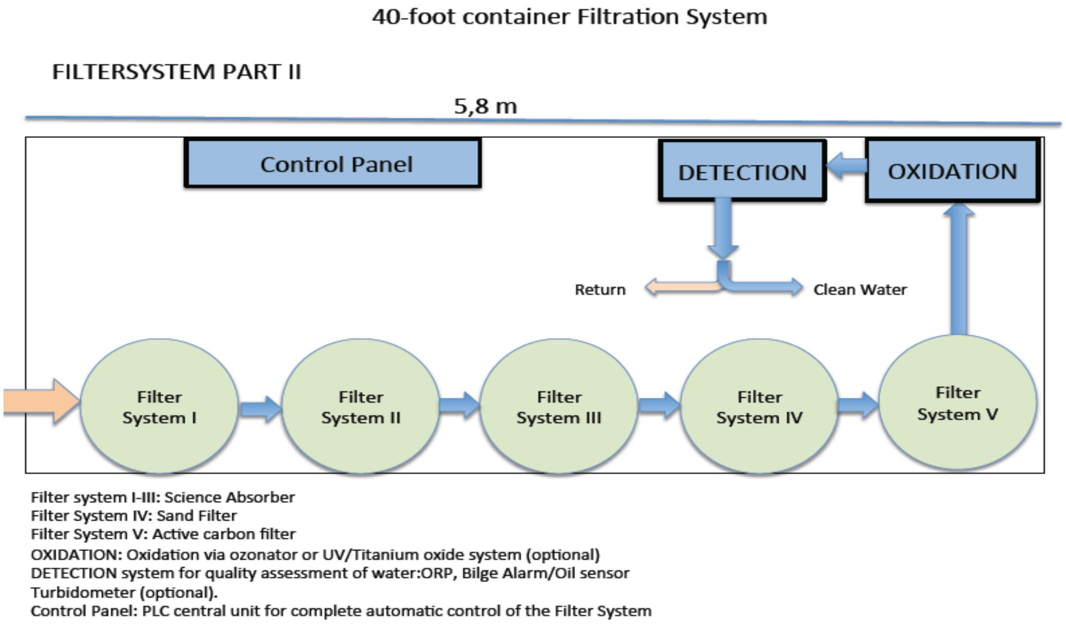
The end-of-pipe SFS solution offers several benefits as highlighted:

1. This technology enables the recovery of about 98% valuable, saleable hydrocarbons from the sludge.
2. The fluidizing oil is a petroleum cutter stock; the recovered oil needs no further treatment before it is carried to the production.
3. The unmanned concept of this technology means that nobody needs to enter the tank during cleaning operations, thereby ensuring the utmost personnel safety. During washing, the atmosphere within the hydrocarbon crude oil tank is continuously monitored to guarantee that it does not become flammable, and nitrogen is used to control it. To this end, the unit is equipped with O_2–monitoring system and alarm.



Öckerö Container C2:
Oil separator
Tank and pump
7-bag filter with Science Absorber (3 items)
Flocculation box (Flock)
Screwpump with pressure sensor
Bag filters (10 micrometer filter bags)
Sand and carbon filters
Neutralisation tank

Fig. 4. End-of-pipe SFS separation system I



Filter system I-III: Science Absorber
Filter System IV: Sand Filter
Filter System V: Active carbon filter
OXIDATION: Oxidation via ozonator or UV/Titanium oxide system (optional)
DETECTION system for quality assessment of water:ORP, Bilge Alarm/Oil sensor
Turbidometer (optional).
Control Panel: PLC central unit for complete automatic control of the Filter System

Fig. 5. End-of-pipe SFS separation system II

4. This technology is environmentally–friendly: during operations no chemicals are used, the process minimises hydrocarbon emissions due to closed-loop cleaning and substantially reduces liquids and solid wastes.
5. The treatment is efficient; offering desludging, tank cleaning and oil recovery in one integrated process.
6. Cost Savings, The technology recovers more than 98% of the hydrocarbon phase contained within the sludge, which is returned to the client together with the fresh oil used to fluidise it. Such result

generates a significant cost saving that is evidenced only by evaluation of the entire cleaning project. Sometimes, comparing the offer for manual cleaning with the offer for recovery operations, it might appear that using this technology is more expensive.

7. The operation during the washing phase of the sludge is treated at a speed of approximately 230,000 kg/day depending on the type of sludge. There is, therefore, a significant reduction of tank down-time.

8. Thus, the recovery method is very flexible since utilities such as power, steam and nitrogen are on site to minimise the cost to the operator [24].

Description of the Science Filtration System – Field Data Collation System and Refinery Location

The Port Harcourt refinery located at Alesa-Eleme, Rivers State, Nigeria, like other refineries around the world, has the problem of oil sludge generation in their crude oil storage tanks. The six 64,000–mm diameter crude oil storage tanks in the refinery contain oily sludge of an average height of 0.6 m each, giving an estimated total volume of sludge in the storage tanks to be approximately 11,581 cubic metres. The sample used for this research work was collected from the Port Harcourt refinery's crude oil tank 50–TK01F. The tank is a floating roof tank of networking capacity 60,000 cubic metres, 64,000–mm diameter, and 21,000 mm height. The design temperature and pressure are 25°C and 1 atm respectively. The crude oil processed in the refinery is Bonny light crude. The oily sludge formed is flowable sludge, of height 0.8 m, giving a total sludge volume of 2570 cubic metres in the tank. The technologies to handle sludge should not disrupt the refinery processes. The oily sludge is characterised for its chemical and physical properties before a design of the end-of-pipe sludge process is carried out. This is because the chemical compositions of oily sludge vary depending on crude oil source, processing scheme, and equipment and reagents used in refining process. The result of this difference in chemical compositions of the oily sludge, its physical properties such as density, viscosity, and heat value equally vary significantly [4].

Materials and Methodology

Materials

The principal material used in this investigation is oily sludge. The end-of-pipe science filtration system consists of pump, 2 containers (which is constructed as one 40-foot container each), 3 sedimentation tanks, with total capacity of up to 2500 L, 3 level detectors for the sedimentation tanks, 2 chemical tanks with detectors, 1 oil separator with oil detection and level alarm system, 1 reservoir middle tank and pump, 1 level sensor and programmed pump operation under programming logic controller (PLC), three 7–bag filters with the science absorber (15 L absorber/bag, totalling 105 L absorber per item and 315 L in summation), 1 flocculation tank with automatic pH dependent dispenser of flocculation chemicals, 1 infra-red (IR) level sensor in flocculation tank that operates screw pump activity, 1 screw pump, 1 pressure sensor to monitor the status of filters (three 1-bag filters, 1 sand filter and 2 active carbon filters), 1 conductivity sensor, 1 oil detection system. The system is controlled by a Siemens PLC using the company's code with menu system. Power is supported by a 340V 3-phase system. The flow capacity is 4–10m^3/h.

Absorber capacity of SFS

At half the volume of oil, it implies a maximum capacity of about 150 L oil can be trapped by the system. This is an indication that oil-in-water (OiW) at 5 ppm in the water will saturate the filter material after a total flow of about 30000 m^3 of water flow before a change of filter material is needed. At a flow of 10 m^3/h, saturation is reached after 125 days (which is approximately 4 months). At 10 ppm OiW, the filters will need to be changed after approximately 60 days (2 months).

For the metal absorption, the science absorber material has a capacity to bind ionised metals. The absorption rate varies depending on the conditions, e.g., 6–40 g Cu or Zn/kg absorber material or 20-120 g Pb/kg absorber material.

Sludge Collection System: Adding a Centrifuge to the Science Filter System

In cases where a high amount of sludge is expected, the use of a centrifuge system may be required. The centrifuge system can be chosen, depending on the flow and sludge characteristics. To determine the most optimal solution, it is important to have samples of the water to be processed. The samples are analysed and a proper system is suggested. The centrifuge models available and their characteristics are given in Table 1. The proposed model for the application at 10 m^3/h is the DC10 model from a list of several models designs (LP1, LP5, DC3, DC6, DC10, DC12, DC20, and DC40) presented by SGE, shown in Table 1. The space considerations are depicted in Fig. 6.

Table 1. Design Specifications of the end-of-pipe technology by centrifugation as presented by SGE

Model	**LP1**	**LP5**	**DC3**	**DC6**	**DC10**	**DC12**	**DC20**	**DC40**
			Dewatering principle					
Concurrent configuration	No	No	Yes	Yes	Yes	Yes	Yes	Yes
Counter-current configuration	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
			Operation data (optional)					
Electrical operation	Yes	Yes	Yes	Yes	Yes	Yes	Yes	-
Hydraulic operation, screw,	-	-	Yes	Yes	Yes	Yes	Yes	Yes
Motor output installed for drum (kW)	7.5 1)	11 1)	7.5-15	11-30	11-30	15-30	15-37	55
Motor output for screw (kW)			5.5-7.5	5.5-7.5	7.5-15	7.5-15	7.5-18.5	30
			Materials					
High-strength steel	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Acid-resistant stainless steel (optional)	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Machine Colour (optional)	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Wolfram carbide coating	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
			Capacity					

Volume capacity (m^3/h)	1-3	4-6	1-5	3-10	5-18	6-23	8-35	25-65
Maximum absorber material (kg)	50	150	120	250	500	600	800	1600
Dimensions &weight, approx. values								
Length, L (mm)	1900	2600	2800	3400	3300	3700	4000	4800
Max., W (mm)	900	1235	1000	1000	1200	1100	1200	1500
Height, H (mm)	765	840	1500	1500	1500	1600	1600	1700
Distance between legs, I (mm)	1700	1770	2100	2600	2400	2900	3200	3700
Lowest lifting hook height, K (m)	1.4	1.4	2	2	2	2	2	2
Rotor weight (kg)	200	600	600	800	900	700	1100	2800
Total weight (kg)	750	1350	1800	2100	2600	2500	3100	6800

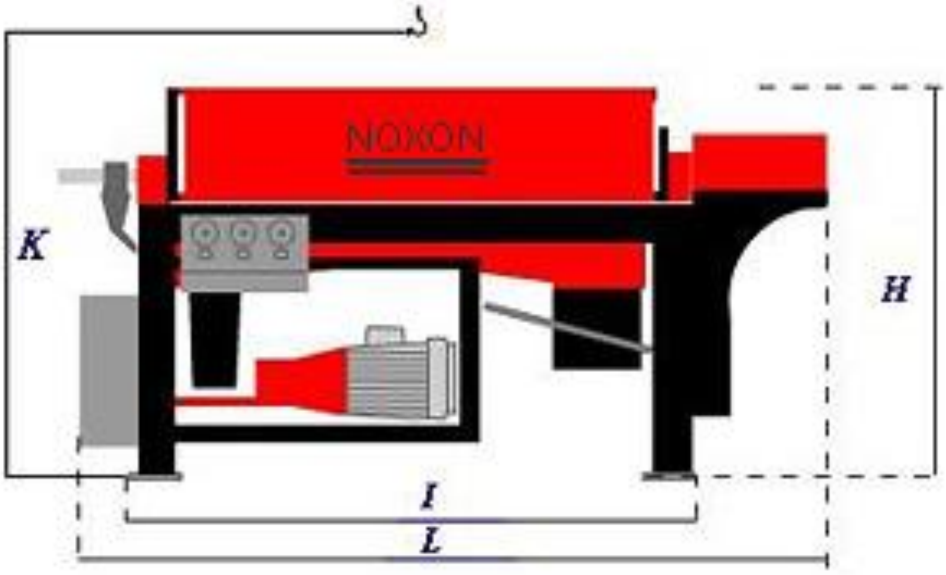


Fig. 6. Space considerations

Other ways to effectively reduce the space needed is to alter the filtration system. For example, the flocculation may be done prior to the centrifuge dependent on filtration steps. This will take away the need of sedimentation tanks.

Additional Items

The following items are not included in the base offer and are specified only for information. A special quote for these items may be requested if there was a specific need.

1. External power generator: To power the filter system in remote areas.
2. Insulated container and air conditioning system to keep temperature constant. Most electronic systems may work poorly at temperatures below 0^{o}C and above 50^{o}C.

Methodology

The oil sludge was collected from the crude oil storage tank 50-TK01F after dewatering of the crude oil storage tank at the Port Harcourt Refining Company, Alesa-Eleme, Rivers State, Nigeria. The sludge was a thick viscous but flowable sludge. About 4 L of oil sludge was collected in laboratory sample bottles and later transferred into a plastic can for preservation and storage. Gas chromatography was used to measure qualitative and quantitative analyses of the petroleum hydrocarbon content of the sludge. The empirical data collation and analysis involved the following steps:

(i) The mobile phase, which is the helium gas, is a stationary phase is the column. The sample extracted is placed on the injector tray; the injector transfers the sample onto the liner from where the mobile phase drives the sample into the column, and the sample is separated into its various components. The concentrations of the analytes were measured by calibrating the instrument with pure standard of the analytes of a known concentration. The composition of the sample displayed on the computer panel was recorded. For the aliphatic hydrocarbons, the analysis was run at an initial temperature of 40°C for 2 min to a final temperature of 240°C to hold for 20 minutes. The total run time was 38.667 min. For the aromatic hydrocarbons, the analysis was run at an initial temperature of 60°C for 1 min to a final temperature of 300°C for hold for 3 min. The final run time was 28 min.

(ii) For the sample preparation, 5g of the sludge sample was treated with 10 mL of dichloromethane in a separating funnel. The mixture was vigorously shaken for 45 min and allowed to stand on a retort stand for 30 min for the layers to be separated thereby the hydrocarbon content was extracted. The dichloromethane extract was decanted into a beaker and exposed to the atmosphere for 2 min to concentrate the hydrocarbons present in the sample. The sample was further treated by inserting a cotton wool soaked in anhydrous sodium tetraoxosulphate (VI), Na_2SO_4, and filtering the remaining extract through it to absorb the water present in the extract. Then, the filtrate collected was used for the GC analysis. The model of the gas chromatograph used is Agilent Technologies 7890A. The model of the detector used is Agilent Technologies 5975C, while the model of the injector used is Agilent Technologies 7633B series. The aromatic and aliphatic hydrocarbons were prepared in the following concentrations: 62.4 ppm, 125 ppm, 250 ppm and 500 ppm to calibrate the instrument. The principle of GC analysis is the principle of separation techniques where there is a mobile phase and a stationary phase for separation to occur.

The water content of the sludge was determined using the Dean and Stark method (ASTM D95) [25]. 200 mL of the sludge sample was treated with a precipitating reagent. After the precipitate was formed, it was allowed to digest and the solution was carefully filtered. The filtrate was heated and the water present was vaporised, condensed and collected in a graduated collection tube to determine the volume of water in the sludge.

The amount of solid in the sludge was determined by placing dried samples at 105°C in a furnace at 550°C for 120 min [25]. The residue shows the solid content, SC, of sludge as weight percent as follows:

$$SC = \left(W_R / W_S \right) \times 100\% \tag{1}$$

where W_R is the weight of residue remaining after burning (g), and W_S the mass of tested sample (g).

The volume of oil in the sludge was determined by carrying out a total volume balance after determination of water content and solid content as follows [25]:

$$\text{Total petroleum hydrocarbon} = 100\% - (\text{water content in wt }\% + \text{solid content in wt }\%) \tag{2}$$

For the cloud point determination, the apparatus was set up as shown in Fig. 7. The cloud point was determined at the temperature at which a “cloudy” (waxy crystals) formation just appears at the surface of the test tube.

The pour point of the sludge was determined at the temperature at which the sludge ceases to flow when the test tube is tilted.

The viscosity of the sludge was determined using a rheometer. The spindle type used was spindle 00 for 500 mL of sludge placed in a 600 mL beaker. The rheometer speed was varied from 50 rpm to 100 rpm with 10 rpm intervals, and the dynamic viscosity at these various speeds were recorded in mPa.s.

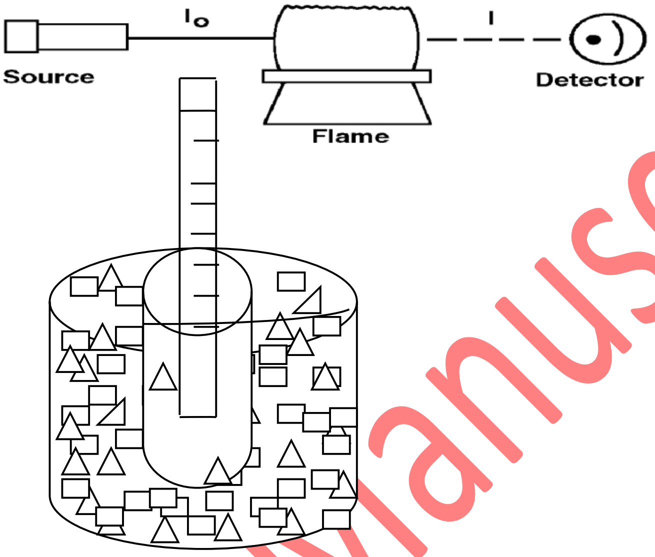


Fig. 7. Cloud point and cloud point determination apparatus

For the determination of metals content of the sludge, 2 g of the sample was weighed into a conical flask with 10 mL of HNO_3 added and gently heated on a hot plate. Heating was then continued until the brown fumes turned to white. The flask was brought down to cool to room temperature. The mixture was rinsed with 20 mL of deionised water and filtered using Whatman qualitative filter paper No. 1 into a standard 25 mL volumetric flask and made up to mark in readiness for atomic absorption spectrometry (AAS) analysis. The stock standard was prepared by weighing 1.5985 g of Pb and dissolving in 1 L of 5% HNO_3, obtained using Eqn. (3):

$$m = M_P / M_L \tag{3}$$

where m is the mass of 1 mol of Pb in $Pb(NO_3)_2$, obtained as 1.299 g/mol Pb using Eqn. (3), M_P and M_L the molar masses of $Pb(NO_3)_2$ and Pb, which are 331.2098 g/mol and 207.2 g respectively.

The stock standard prepared was serially diluted to concentrations of 5 ppm, 10 ppm, 15 ppm, 20 ppm, 25 ppm. These different calibrations levels were used to generate a suitable curve, which was used to calibrate the instrument. After the serial dilution of the stock standard, the different calibrants were fed into the AAS as standard samples. The atomic absorption process uses light at the resonance wavelength of initial intensity, I_0, which is focused on the flame cell containing ground state atoms. The initial light intensity was decreased by an amount determined by the atom concentration in the flame cell. The light is then directed onto the detector where the reduced intensity, I, is measured. The amount of light absorbed is determined by comparing I to I_0.

For the natural sludge organic (NSO) determination, the organic phase was extracted by mixing the oily sludge with methylene chloride (i.e., dichloromethane, CH_2Cl_2) at room temperature for 24 h. After extraction, the solvent was removed in a rotary evaporator. The nitrogen contents in the aqueous and organic phases of the NSO was determined by chemiluminescence. The sulphur content was determined by ASTM D4294 standard test method for sulphur in petroleum and petroleum products by energy-dispersive X-ray fluorescence spectrometry. The oxygen content was determined using ASTM E-385 using the 14-MeV neutron activation and direct counting technique. This test method is independent of the chemical form of the oxygen.

Results and Discussion

Laboratory Results

Table 2 shows the gas chromatograph results for the aliphatic hydrocarbons in the crude oil sludge from Port-Harcourt refinery.

Table 2. Gas chromatography for the aliphatic hydrocarbons in the oily sludge sample

S/No.	Compound	Retention time, RT (s)	Qion	Response	Concentration × 10^4 (ppm)	Deviation (min)
1.	Decane	7.443	57	97964	2.62	95
2.	Undecane	8.931	57	113066	2.82	94
3.	Dodecane	10.315	57	116440	2.74	94
4.	Tridecane	11.614	57	150500	3.42	94
5.	Tetradecane	12.827	57	161492	3.58	88
6.	Pentadecane	14.063	57	11792	0.25	75
7.	Hexadecane	15.145	57	23879	0.54	85
8.	Heptadecane	16.135	57	413355	10.78	82
9.	Pentadecane 2,6,10,14...	16.135	57	413355	9.51	83
10.	Octadecane	17.136	57	165609	3.60	89
11.	Hexadecane, 2,6,10,14-...	17.136	57	165609	4.13	95
12.	Nonadecane	18.063	57	5536	0.12	16
13.	Eicosane	18.841	57	153182	3.69	94
14.	Heneicosane	19.785	57	172127	3.72	96
15.	Heptadecane	20.878	57	123647	No calibration	-
16.	Tetracosane	23.882	57	97820	4.16	95
17.	Heptadecane	26.034	57	100303	No calibration	-
18.	Hexacosane	28.832	57	83852	2.36	95
19.	Heptacosane	0		0	Not determined	-
20.	Tetracosane	37.289	57	41741	No Calibration	-

The laboratory results of the compositions of the oily sludge from Port-Harcourt refinery are: nitrogen (0.17 wt%), sulphur (0.21 wt%), oxygen (2.15 wt%), moisture content (23.4 wt%), total petroleum hydrocarbon (51.62 wt%), and total solids (24.98%). These results are within the range specified for contents of water (30 – 85 wt %), total petroleum hydrocarbon (5 – 86.2 wt%) and total solids (5 – 46 wt%), as reported by Hu et al. (2013). The metals in the solid fraction are: iron, Fe (24.35 mg/kg), copper, Cu (21.67 mg/kg), lead, Pb (10.60 mg/kg), cadmium, Cd (13.48 mg/kg), chromium, Cr (93.21 mg/kg) and nickel, Ni (123 mg/kg). The metal content of the oily sludge also falls within the range given by American

Petroleum Institute [28], and lower than higher concentration of metals in petroleum sludge from refineries reported as Zn (1,299 mg/kg), Fe (60,200 mg/kg), Cu (500 mg/kg), Cr (480 mg/kg), Ni (480 mg/kg), and Pb (565 mg/kg) [29–32].

Table 3 shows the gas chromatography results for the aromatic components in the oily sludge from Port-Harcourt refinery.

Table 3. Gas chromatography result for the aromatic hydrocarbons in the sludge sample

S/No..	Compound	R.T. (s)	Qion	Response	Concentration	Deviation (min)
1.	Naphthalene	7.996	128	2102	10.08 ppm	80
2.	Acenaphthylene	11.687	152	53	9.68 ppm	63
3.	Acenaphthene	12.093	153	94	9.24 ppm	36
4.	Fluorene	13.312	166	223	0.00 ppm	58
5.	Phenanthrene	15.566	178	1046	8.02 ppm	68
6.	Phenanthrene	15.664	178	1035	No Calib	
7.	9,10-Anthracenedione	17.523	208	1211	0.06 ppm	28
8.	Fluoranthene	18.404	202	891	0.00 ppm	71
9.	Pyrene	18.919	202	1039	0.00 ppm	63
10.	Triphenylene	21.803	228	408	0.00 ppm	56
11.	Triphenylene	21.895	228	368	No Calib	
12.	Benz[e]acephenanthrylene	24.235	252	59	0.00 ppm	1
13.	Benz[e]acephenanthrylene	24.287	252	291	No Calib	
14.	Benz[e]acephenanthrylene	24.893	252	554	No Calib	
15.	Benzo[ghi]perylene	27.451	276	191	٠,٠ ppm	72

Figs. 8 and 9 shows the gas chromatography for the hydrocarbons in the oily sludge sample from Port-Harcourt refinery.

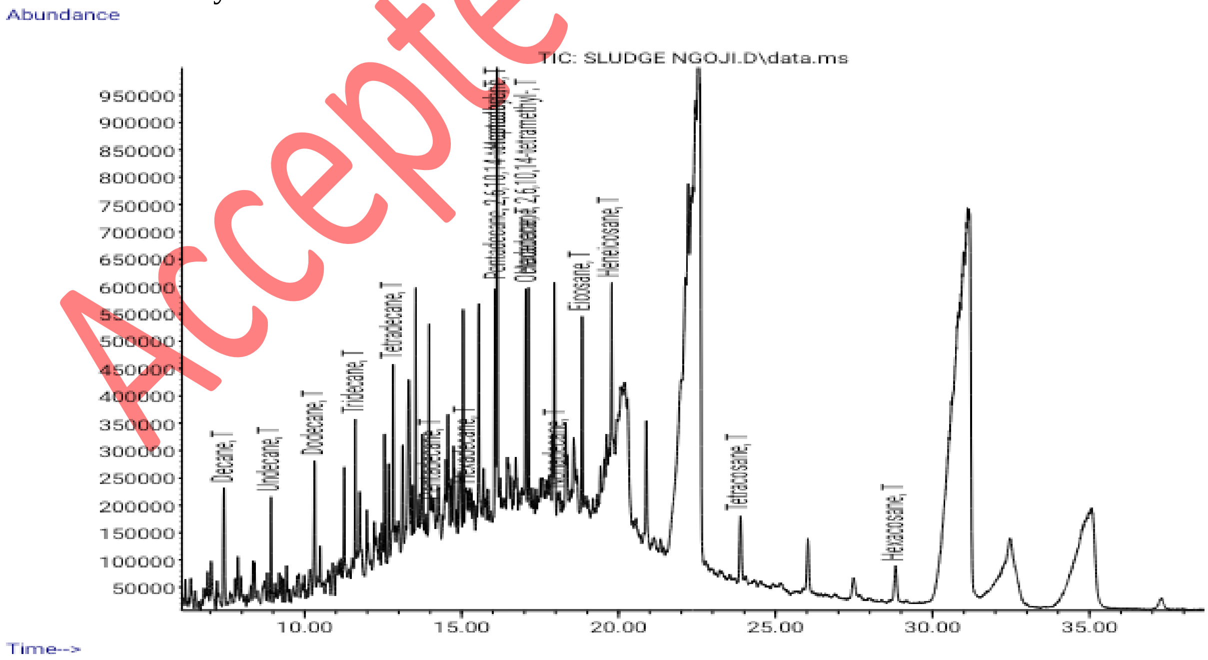


Fig. 8. Gas chromatography results for the aliphatic hydrocarbons in the sludge sample

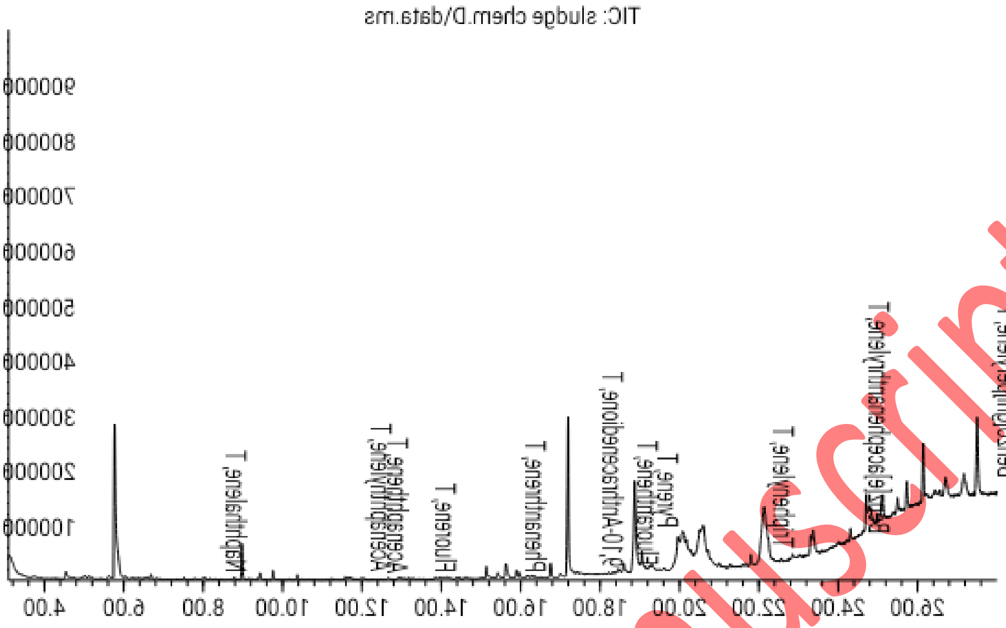


Fig. 9. Gas chromatography result for the aromatic hydrocarbons in the sludge sample

Table A1 in the appendix is the laboratory analysis results converted to mass flow rate (basis: 100 kg of sludge) and the corresponding mass fraction.

Computer Simulation Results and Design Specifications

Fig. 10 shows proposed design of the end-of-pipe technology (hydrocyclone) process flow diagram, where the two streams of sludge and kerosene cut are fed into a paddle mixer and then introduced into the heat exchanger. The streams are pumped through a centrifugal pump into the hydrocyclone where the solids are separated from the oily sludge water and the crude oil is recovered from the separator. The results for the ChemCad simulation flow for the proposed design of the end-of-pipe technology (hydrocyclone) shown in Fig. 10 are presented in Tables A2 to A4 in the appendix.

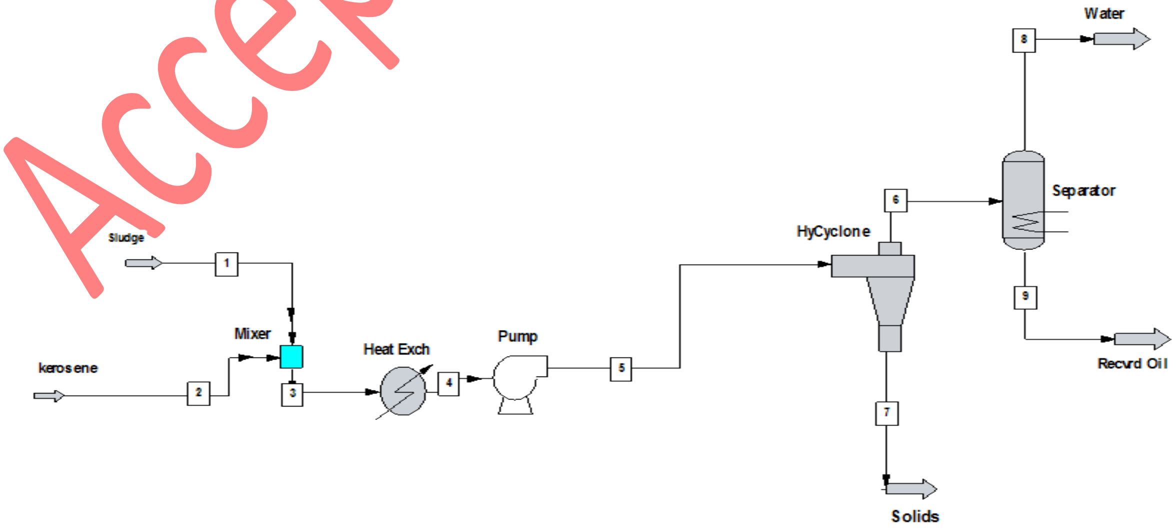


Fig. 10. End-of-pipe technology (hydrocyclone) process flow diagram

Table A2 shows the computer model simulation basis for streams 1 to 9, which are numbered accordingly in Fig. 10. The recovery rate of the crude oil from the sludge using proposed design is 97.9%. Tables A3 and A4 show the computer simulation flow summaries in kg/h and mass fraction respectively of the gas, metallic and hydrocarbon components in the sludge for streams 1 to 9. The hydrocyclone underflow contains solid separated from the sludge. This solid has the composition by mass of hydrocarbons and water to be 3.8% and 4.06% respectively. The hydrocarbon content of the hydrocyclone overhead recovered via the component separator bottoms contains 97.9 % mass of hydrocarbon, 1.5% mass of water and 0.9% mass of solids. The component separator top is the water stream separated from the hydrocarbon. The results show that this stream contains a negligible amount, less than 1% of hydrocarbons. Thus, the stream is sent to a wastewater filter system for further treatment. The hydrocarbon phase of the sludge is fluidized by injecting kerosene cuts that are compatible with the sludge to be cleaned. A higher hydrocarbon recovery of 97.9% with a sludge-solvent ratio of 1:4 (sludge in gram: solvent in mL) was obtained. Sludge fluidization is determined by the chemical action of the heated kerosene cut, and by the mechanical action of jet washers that are installed on the tank roof. Two feed streams to the mixer, sludge and kerosene, were properly specified and charged to the mixer at the rates of 10,000 kg/h and 40,000 L/h respectively. An output pressure of 14.7 psia was specified for the mixer. The sludge/kerosene mixture was charged to the heat exchanger where the stream temperature was raised to 70°C and suctioned to the hydrocyclone via a centrifugal pump. The hydrocyclone was set to design mode. The required overall efficiency, allowable pressure drops of 10 psia and maximum cyclone diameter were specified. The hydrocyclone dimensions were calculated by the software at the RUN command. The pump outlet pressure was specified with reference to the hydrocyclone pressure drop to keep the hydrocyclone overflow pressure near atmospheric pressure to enhance the cyclone performance. The ChemCad is used to compute the Net Positive Suction Head Available (NPSHa), power required for the pump, outlet pressure, head of the pump, and liquid volumetric flow rate of the inlet stream. The underflow of the hydrocyclone was the solids separated from the sludge/kerosene stream by the hydrocyclone. The hydrocyclone overhead was the liquid stream, which was charged to a component separator to separate the water from the hydrocarbons. The specification for the component separator was based on the top stream bubble point temperature and pressure drop across the unit. Split fractions for the top stream components were specified. The ChemCad software calculates the heat duty for the component separator at the RUN command. The top stream of the component separator was the water stream to be sent to the wastewater treatment unit. The bottom stream of the component separator is the recovered oil, which is sent for laboratory analysis and then returned to refinery process line if they meet the tank owner's specifications.

Computer Simulation Equipment Design Specifications

The results show a hydrocarbon recovery rate up to 97.9 % by our proposed end-of-pipe technology. Table 4 shows the results summary of the stream flow composition of sludge and kerosene fed in the end-of-pipe system shown in Fig. 10.

Table 4. Stream flow compositions of sludge and kerosene feeds

	Mass flowrates of various compositions (kg/h)			Total mass flow (kg/h)
Streams	**Hydrocarbons**	**Water**	**Solids**	
Sludge feed	5028.2841	2397.46	2574.255	10000.00
Kerosene feed	30119.9579	0	0	30119.9579
Hydrocyclone underflow	104.2221	111.587	2530.122	2745.9308
Hydrocyclone overflow	35044.0187	2285.873	44.1337	37374.0257
Component separator top stream	0.023626132	2217.297	0	2217.320726

Component separator bottom stream	35043.99507	68.5762	44.1337	35156.70497

The design specification of the paddle mixer is equipment #1 with an output pressure of 14.7 psia while the design specifications for the heat exchanger, hydrocyclone, pump and component separator are presented in Table 5.

Table 5. Heat exchanger, hydrocyclone, pump and component separator specifications

Specifications	**Heat exchanger**	**Hydrocyclone**	**Pump**	**Component separator**
Equipment No.	2	3	4	5
1st Stream, T_{out} (°C)	70			
1st Stream, p_{out} (psia)	14.7			
Calculated Heat Duty (MMBtu/h)	3.666			
LMTD Corr Factor	1			
Mode		1		
Alpha		0.45		
Exponent		0.8		
Particle diameter (micron)		8		
Max. diameter (ft)		45		
Allowable pressure drop (psi)		10		
Cyclone diameter (ft)		0.7713		
No. of cyclones		3		
Inlet diameter (m)		0.1429		
Length (m)		5		
Overflow diameter (m)		0.2		
Underflow diameter (m)		0.15		
Cone angle		20°C		
D50- microns		7.246		
Efficiency		0.8773		
Pressure drop (psi)		9.7283		
Output pressure (psia)			24.7	
Efficiency			1	
Calculated power hp			1.361	
Calculated p_{out} (psia)			24.7	
Head (ft)			30.4371	
Volumetric flow rate (L/h)			52939.5352	
Mass flow rate kg/h			40119.957	
Request NPSH calc			1	
Top temp mode				1
Bottom temp Spec				70
Heat duty MMBtu/h				0.2236
Component No. 2				0.001
Component No. 4				0.97

Component No. 5				7.00×10^{-5}
Component No. 6				9.00×10^{-8}
Component No. 11				6.60×10^{-7}
Component No. 18				2.00×10^{-8}

Table 6 compares the results obtained from simulating the design of the end-of-pipe technology using centrifugation with those obtained using hydrocyclone.

Table 6. Key performance results

Key parameters for sludge treatment technology	**End-of-pipe technology**	
	Centrifuging	**Hydrocyclone**
Feedstock intake capacity	3.62 m^3/h	11.27 m^3/h
Processing of 10,000 m^3	≈4 months	≈1 ½ month
Hydrocarbon crude oil recovery	75%	97.9%
Hydrocarbon content in solid waste	> 10%	3.8%
Hydrocarbon content in waste water	15%	< 1%
Solids content in recovered oil	-	0.9%
Water content in recovered oil	-	1.5%

It can be seen in Table 6 that it would take less duration to process 10,000 m^3 of oily sludge using the end-of-pipe hydrocyclone technology than using centrifugation technology. The end-of-pipe technology using centrifugation has a 75% hydrocarbon crude oil recovery, no solids content and water content in the recovered oil while the hydrocarbon content of the hydrocyclone overhead recovered via the component separator bottoms contains 97.9% mass of hydrocarbon, 0.9% mass of solids and 1.5% mass of water. The extra unit filtration system in the end-of-pipe system using centrifugation technology may have contributed to zero solids and water contents in the recovered oil. The hydrocarbon contents in solid for the end-of-pipe technology using hydrocyclone and centrifuging contain 3.8% and less than 10%. Hence, the end-of-pipe technology (hydrocyclone) has better performance than the end-of-pipe technology (centrifugation) owing to higher hydrocarbon crude oil recovery. This is probably due to the use of natural hydrocarbon solvent (kerosene) to improve the extraction process of the hydrocarbon oil in sludge. Moreover, the proposed end-of-pipe technology (hydrocyclone) in this study has the capacity to handle large volume of crude oil sludge, thus reducing the overall storage tank down time during tank cleaning processes. However, the processes involved in the end-of-pipe technology applied to treat crude oil sludge in this study do not address the problem of heavy metals contained in the sludge cake to be disposed of. Thus, it is recommended that further work should be done to find an appropriate bioremediation solution to handle the heavy metals prior to the solid waste disposal. The bioremediation can then be an additional module to complete this proposed end-of-pipe technology.

Conclusions

The modelling of an end-of-pipe technology (hydrocylone) to treat oily sludge from Port-Harcourt refinery in Nigeria is presented. The hydrocarbon oily sludge was characterised and analysed using gas chromatography for the aliphatic and aromatic hydrocarbons, together with the composition of solids metallic and water content of the sludge**.** The results for the ChemCad simulation flow for the design of the proposed end-of-pipe technology are presented for the equipment specifications, computer simulation flow and computer simulation model basis. The results obtained are compared with the end-of-pipe technology (centrifugation) with science filtration system as developed by a company in Sweden (Scandinavian green Export, SGE). The solids in the underflow from the cyclone contain about 3.8% by mass hydrocarbons and 4.06% water by mass. The hydrocarbon content of the hydrocyclone overhead recovered via the component separator bottoms contains 97.9 % mass of hydrocarbon, 1.5% mass of water and 0.9% mass of solids. However, the end-of-pipe technology using centrifugation is designed for 75% hydrocarbon oil recovery, no solids or water content in the recovered oil. The extra unit filtration system incorporated in the end-of-pipe system using centrifugation technology as proposed by SGE may have contributed to zero solids and water contents in the recovered oil. Hence, the end-of-pipe technology (hydrocyclone) has better performance of higher hydrocarbon oil recovery than the end-of-pipe technology (centrifugation) probably due to the use of natural hydrocarbon solvent (kerosene) to improve the extraction process of the hydrocarbon oil in sludge. Equally, the design end-of-pipe technology deployed for crude oil sludge treatment in this work meets the requirements for high quality oil recovery, environmental and personnel safety, economic viability and applicability. However, the processes involved in the end-of-pipe technology applied to treat crude oil sludge in this work do not address the problem of heavy metals contained in the sludge cake to be disposed of. It is thus recommended that further work should be done to find an appropriate bioremediation solution to handle the heavy metals prior to the solid waste disposal. The bioremediation can then be an additional module to complete this proposed end-of-pipe technology.

Statements and Declarations

Conflict of Interest: The authors declare that there is no conflict of interest regarding the publication of this article.

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Appendix A: Laboratory results, computer model simulation basis, computer simulation flow summaries in kg/h and mass fractions.

Table A1. Laboratory analysis results converted to mass flow rate (basis: 100 kg of sludge)

Component	mass of component in sludge (kg)	mass fraction of components in sludge
Oxygen	2.14644	0.0214644
Nitrogen	0.17	0.0017
sulphur	0.21	0.0021
decane	1.350872	0.01350872
undecane	1.453992	0.01453992
dodecane	1.402432	0.01402432
tridecane	1.763352	0.01763352
tetradecane	1.845848	0.01845848
pentadecane	0.1289	0.001289
hexadecane	0.278424	0.00278424
heptadecane	5.558168	0.05558168
pentadecane 2, 6, 10, 14	4.903356	0.04903356
octadecane	1.85616	0.0185616
hexadecane 2, 6, 10 14	2.129428	0.02129428
nonadecane	0.061872	0.00061872
eicosane	1.902564	0.01902564
heneicosane	1.918032	0.01918032
tetracosane	2.144896	0.02144896
hexacosane	1.216816	0.01216816
naphthalene	5.197248	0.05197248
acenaphthylene	4.991008	0.04991008
acenaphthene (biphenyl) $C_{12}H_{10}$	4.764144	0.04764144
phenanthrene	4.135112	0.04135112
anthracenediol, $C_{14}H_8O_2$ (rep by dodecene)	0.030936	0.00030936
Iron	0.000608263	6.08263E-06
copper	0.000541317	5.41317E-06
lead	0.000264788	2.64788E-06
cadmium	0.00033673	3.3673E-06
chromium	0.002328386	2.32839E-05
nickel	0.00307254	3.07254E-05
vanadium	9.19264E-05	9.19264E-07
sand (SiO_2)	24.97275605	0.24972756
moisture H_2O	23.46	0.2346
	100.0000000000	1

Table A2. Computer model simulation basis

CHEMCAD 6.1.4					Page 1				
Job name:	NG2	Date:	10/01/2024	Time:	18:33:06				
STREAM PROPERTIES									
Stream No.	1	2	3	4	5	6	7	8	9
Name	Sludge	kerosene	Sludge+ Kerosene	Heated Mix	Pump Outlet	Cyclone overhead	Solids	Water	Recovered oil
- - Overall - -									
Molar flow (kmol/h)	160.9803	176.8247	337.8049	337.8049	337.8049	268.673	69.132	102.8896	165.7833
Mass flow (kg/h)	10000	30119.958	40119.9581	40119.958	40119.9581	30241.358	9878.5933	1853.5692	28387.791
Temp (°C)	25	25	24.9791	70	70.0722	70.0722	70.0722	100.2242	70
Pressure (psia)	14.7	14.7	14.7	14.7	24.7	14.9717	14.9717	14.9717	14.9717
Vapor mole fraction	0.003744	0	0.0007049	0.001528	0.0003312	0	0	0	0.002411
Enth MMBtu/h	-41.322	-58.887	-100.21	-96.543	-96.54	-76.949	-19.594	-27.338	-49.388
Tc (°C)	442.8315	385.1	395.3885	395.3885	395.3885	395.3885	395.3885	374.1964	396.5759
Pc (psia)	4431.3018	263.0573	1581.535	1581.535	1581.535	1581.537	1581.5359	3207.9219	335.4297
Std. sp gr. wtr = 1	0.946	0.753	0.793	0.793	0.793	0.777	0.849	1	0.765
Std. sp gr. air = 1	2.145	5.881	4.101	4.101	4.101	3.886	4.934	0.622	5.912
°API	18.0972	56.415	46.8642	46.8642	46.8642	50.7173	35.0687	10.0005	53.3759
Average mol wt	62.1194	170.338	118.7667	118.7667	118.7667	112.5582	142.8947	18.0151	171.2343
Actual dens (kg/m^3)	400.2402	745.028	708.4881	595.7042	732.1279	740.6068	815.742	957.6345	568.916
Actual vol (m^3/h)	24.985	40.428	56.6276	67.3488	54.7991	40.8332	12.1099	1.9356	49.898
Std liq (L/h)	10572.257	40000	50572.253	50572.253	50572.253	38943.514	11628.736	1853.578	37089.936
Std vap @ 0°C (m^3/h)	3608.1552	3963.2856	7571.4399	7571.4399	7571.4399	6021.9411	1549.5001	2306.1322	3715.8078
- - Vapor only - -									
Molar flow (kmol/h)	0.5978		0.2372	0.5141	0.1114				0.3985
Mass flow (kg/h)	16.5667		6.5759	13.1046	2.9545				10.1752
Average mol wt	27.7149		27.7253	25.488	26.511				25.5357
Actual dens (kg/m^3)	1.1336		1.1341	0.9072	1.5846				0.9257
Actual vol (m^3/h)	14.6144		5.7984	14.4444	1.8646				10.9915
Std liq (L/h)	20.4213		8.1063	15.5688	3.5724				12.0986
Std vap @ 0°C (m^3/h)	13.3978		5.3161	11.524	2.4979				8.9311
Cp (kJ/(kg K))	1.0605		1.0608	1.2662	1.1719				1.2618
Z factor	0.9997		0.9997	0.9981	0.9986				0.9982
Visc osity (cP)	0.01745		0.01744	0.01667	0.01789				0.01672
Th cond (W/(m K))	0.0252		0.0252	0.0269	0.0277				0.0269
- - Liquid only - -									
Molar flow (kmol/h)	159.0658	176.8247	336.251	335.974	336.3767	268.1948	68.2934	102.8896	164.9067
Mass flow (kg/h)	7409.178	30119.958	37539.1238	37532.596	37542.749	29925.448	7620.2517	1853.5693	28061.701
Average mol wt	46.5793	170.338	111.6402	111.7128	111.6092	111.581	111.581	18.0151	170.1672
Actual dens (kg/m^3)	887.1738	745.028	769.0861	737.5937	737.356	737.2894	737.2894	957.6345	725.8248
Actual vol (L/h)	8351.4398	40427.954	48810.0444	50885.19	50915.3632	40588.47	10335.496	1935.5707	38661.811

Std liq (L/h)	8532.7029	40000	48545.0095	48537.554	48549.5515	38698.804	9854.3101	1853.578	36833.128
Std vap @ 0ºC (m^3/h)	3565.2452	3963.2856	7536.611	7530.4034	7539.4294	6011.2241	1530.7051	2306.1322	3696.1595
Cp (kJ/(kg K))	2.5985	2.098	2.1964	2.3728	2.3729	2.3732	2.3731	4.2253	2.2522
Z factor	0.003	0.0118	0.0078	0.007	0.0118	0.0071	0.0071	0.0008	0.0106
Viscosity (cP)	1.943	1.407	1.498	0.7549	0.7548	0.7535	0.7535	0.2799	0.7859
Th cond (W/(m K))	0.2154	0.1354	0.1451	0.1348	0.1348	0.1347	0.1347	0.6761	0.126
Surf. tens. (N/m)	0.04	0.0249	0.0271	0.0228	0.0228	0.0228	0.0228	0.0586	0.0215

Table A3. Computer simulation flow summaries (kg/h)

FLOW SUMMARIES

Stream No.	1	2	3	4	5	6	7	8	9
Stream Name	Sludge	kerosene	Sludge+Kerosene	Heated Mix	Pump Outlet	Cyclone Ovflow	Cyclone Undflw	Sep top	Sep bottom
Temp C	25	25	24.9791	70	70.0722	70.0722	70.0722	100.2242	70
Pres psia	14.7	14.7	14.7	14.7	24.7	14.9717	14.9717	14.9717	14.9717
Enth MMBtu/h	-41.322	-58.887	-100.21	-96.543	-96.54	-76.949	-19.594	-27.338	-49.388
Vapor mass fraction	0.002231	0	0.00017514	0.00034903	7.87E-05	0	0	0	0.00036247
Total kg/h	10000.0002	30119.9579	40119.9581	40119.9581	40119.9581	37374.0257	2745.9308	2217.320726	35156.70497
Component kg/h									
Iron	0.0622	0	0.0622	0.0622	0.0622	0.0066	0.0556	0	0.0066
Nitrogen	17.3729	0	17.3729	17.3729	17.3729	13.8469	3.526	0.0138	13.8331
Sulphur	21.4607	0	21.4607	21.4607	21.4607	3.854	17.6067	0	3.854
Water	2397.4603	0	2397.4603	2397.4603	2397.4603	2285.8733	111.587	2217.2971	68.5762002
N-Undecane	148.5885	0	148.5885	148.5885	148.5885	138.4311	10.1574	0.009701659	138.4213983
N-Tridecane	180.2032	0	180.2032	180.2032	180.2032	173.6293	6.5739	0	173.6293
N-Tetradecane	188.6337	0	188.6337	188.6337	188.6337	180.3487	8.285	0	180.3487
N-Pentadecane	514.2641	0	514.2641	514.2641	514.2641	512.8893	1.3747	0	512.8893
N-Hexadecane	246.0668	0	246.0668	246.0668	246.0668	231.1252	14.9416	0	231.1252
N-Heptadecane	568.0083	0	568.0083	568.0083	568.0083	562.7257	5.2826	0	562.7257
N-Octadecane	189.6875	0	189.6875	189.6875	189.6875	188.1886	1.4989	0.000124473	188.1884755
N-Nonadecane	6.3229	0	6.3229	6.3229	6.3229	6.2396	0.0833	0	6.2396
N-Eicosane	194.4298	0	194.4298	194.4298	194.4298	189.9684	4.4614	0	189.9684
n-heneicosane	196.0106	0	196.0106	196.0106	196.0106	191.9284	4.0822	0	191.9284
n-Tetracosane	219.1945	0	219.1945	219.1945	219.1945	215.1069	4.0876	0	215.1069
hexacosane	124.3507	0	124.3507	124.3507	124.3507	114.1126	10.2381	0	114.1126
N-Dodecane	143.3195	30119.9579	30263.2754	30263.2754	30263.2754	30261.0606	2.2157	0	30261.0606
N-Decane	138.0504	0	138.0504	138.0504	138.0504	138.0318	0.0186	0	138.0318
napthalene- 2-et	531.1249	0	531.1249	531.1249	531.1249	531.0281	0.0968	0	531.0281
Copper	0.0553	0	0.0553	0.0553	0.0553	0.001	0.0543	0	0.001
Cadmium	0.0344	0	0.0344	0.0344	0.0344	0.0042	0.0303	0	0.0042
Lead	0.0271	0	0.0271	0.0271	0.0271	0.001	0.0261	0	0.001
Silica	2552.0542	0	2552.0542	2552.0542	2552.0542	40.2553	2511.799	0	40.2553
Nickel	0.314	0	0.314	0.314	0.314	0.0016	0.3124	0	0.0016
Vanadium	0.0094	0	0.0094	0.0094	0.0094	0.0036	0.0058	0	0.0036
Chromium	0.2379	0	0.2379	0.2379	0.2379	0.0064	0.2315	0	0.0064
Biphenyl	486.8643	0	486.8643	486.8643	486.8643	475.8537	11.0107	0	475.8537
Phenanthrene	422.5815	0	422.5815	422.5815	422.5815	411.8146	10.7669	0	411.8146
Acenaphthalene	510.0485	0	510.0485	510.0485	510.0485	504.5294	5.5191	0	504.5294
1-Dodecene	3.1615	0	3.1615	3.1615	3.1615	3.1598	0.0016	0	3.1598
Total kg/h	9999.9996	30119.9579	40119.9555	40119.9555	40119.9555	37374.0257	2745.9308	2217.320726	35156.70497

Table A4. Computer simulation flow summaries (mass fraction %)

FLOW SUMMARIES

Stream No.	1	2	3	4	5	6	7	8	9
Stream Name	Sludge	kerosene	Sludge+Kero	Heated Mix	Pump out	Cyclone Ovflow	Cyclone Undflow	Sep top	Sep bottom
Temp C	25	25	24.9791	70	70.0722	70.0722	70.0722	100.2242	70
Pres psia	14.7	14.7	14.7	14.7	24.7	14.9717	14.9717	14.9717	14.9717
Enth MMBtu/h	-41.322	-58.887	-100.21	-96.543	-96.54	-76.949	-19.594	-27.338	-49.388
Vapor mass fraction	0.002231	0	0.00017514	0.00034903	7.87E-05	0	0	0	0.00036247
Total kg/h	10000.0002	30119.9579	40119.9581	40119.9581	40119.9581	37374.0257	2745.9308	2217.320726	35156.70497
Component mass %									
Iron	0.000622	0	0.000155	0.000155	0.000155	1.76593E-05	0.002024814	0	1.87731E-05
Nitrogen	0.173729	0	0.043302	0.043302	0.043302	0.037049528	0.128408189	0.000622373	0.039346975
Sulphur	0.214607	0	0.053491	0.053491	0.053491	0.010311975	0.641192415	0	0.010962347
Water	23.974602	0	5.97573	5.97573	5.97573	6.116208402	4.063722218	99.99893447	0.195058667
N-Undecane	1.485885	0	0.370361	0.370361	0.370361	0.37039387	0.369907355	0.00043754	0.393726882
N-Tridecane	1.802032	0	0.449161	0.449161	0.449161	0.464572111	0.239405159	0	0.493872506
N-Tetradecane	1.886337	0	0.470174	0.470174	0.470174	0.482550907	0.301719184	0	0.512985219
N-Pentadecane	5.14264	0	1.281816	1.281816	1.281816	1.372314837	0.05006317	0	1.45886624
N-Hexadecane	2.460668	0	0.613328	0.613328	0.613328	0.618411305	0.544136072	0	0.657414283
N-Heptadecane	5.680083	0	1.415775	1.415775	1.415775	1.505659852	0.192379211	0	1.600621277
N-Octadecane	1.896875	0	0.472801	0.472801	0.472801	0.503527775	0.054586226	5.61366E-06	0.535284736
N-Nonadecane	0.063229	0	0.01576	0.01576	0.01576	0.016695017	0.00303358	0	0.017747966
N-Eicosane	1.944298	0	0.484621	0.484621	0.484621	0.508289906	0.16247314	0	0.540347567
n-heneicosane	1.960106	0	0.488561	0.488561	0.488561	0.51353419	0.148663615	0	0.545922606
n-Tetracosane	2.191945	0	0.546348	0.546348	0.546348	0.57555186	0.14886027	0	0.611851708
hexacosane	1.243507	0	0.309947	0.309947	0.309947	0.305325953	0.372846249	0	0.324582751
N-Dodecane	1.433195	100	75.431973	75.431973	75.431973	80.96815912	0.080690307	0	86.07479177
N-Decane	1.380504	0	0.344094	0.344094	0.344094	0.369325481	0.000677366	0	0.392618706
napthalene- 2-et	5.311249	0	1.323842	1.323842	1.323842	1.420848009	0.003525216	0	1.510460381
Copper	0.000553	0	0.000138	0.000138	0.000138	2.67566E-06	0.001977472	0	2.84441E-06
Cadmium	0.000344	0	0.000086	0.000086	0.000086	1.12378E-05	0.001103451	0	1.19465E-05
Lead	0.000271	0	0.000067	0.000067	0.000067	2.67566E-06	0.000950497	0	2.84441E-06
Silica	25.520542	0	6.361059	6.361059	6.361059	0.107709296	91.47349962	0	0.114502483
Nickel	0.00314	0	0.000783	0.000783	0.000783	4.28105E-06	0.011376834	0	4.55105E-06
Vanadium	0.000094	0	0.000023	0.000023	0.000023	9.63236E-06	0.000211222	0	1.02399E-05
Chromium	0.002379	0	0.000593	0.000593	0.000593	1.71242E-05	0.008430657	0	1.82042E-05
Biphenyl	4.868643	0	1.213522	1.213522	1.213522	1.273220348	0.400982428	0	1.353521897
Phenanthrene	4.225814	0	1.053295	1.053295	1.053295	1.101873808	0.392103836	0	1.171368592
Acenaphthalene	5.100485	0	1.271309	1.271309	1.271309	1.349946629	0.200991955	0	1.435087277
1-Dodecene	0.031615	0	0.00788	0.00788	0.00788	0.008454535	5.8268E-05	0	0.008987759
Total kg/h	99.999993	100	99.999995	99.999995	99.999995	100	100	100	100

Appendix B: Calculation of percentage recoveries of oil, solids and water.

$$R_{oil} = \frac{(r_{PHCs} - r_{\text{kerosene}})}{r'_{PHCs}} \times 100$$

where R_{oil} is the % recovery of oil, r_{PHCs} the rate of PHCs in separator bottoms (kg/h), r_{kerosene} the rate of kerosene charged as solvent (kg/h) and r'_{PHCs} the rate of PHCs contained in sludge feed (kg/h).

$$R_s = (r_s / r_{so}) \times 100$$

where R_s is the % of solids in recovered oil, r_s the rate of solids in separator bottoms (kg/h) and r_{so} the rate of solids recovered in oil (kg/h).

$$R_w = (r_w / r_{wo}) \times 100$$

where R_w is the % of water in recovered oil, r_w the rate of water in separator bottoms (kg/h) and r_{wo} the rate of water recovered in oil (kg/h).

The time taken, t, to process 10,000 m^3 of sludge is calculated thus:

$$t = \frac{1 \times 10^4 \, m^3}{Q_f \, m^3 / h} \times \frac{1 \, day}{24 \, h}$$

where Q_f is the feedstock intake capacity (m^3/h).