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Research Article

DEVELOPMENT OF A COMBINED TREATMENT TECHNOLOGY BY CENTRIFUGE AND SOFT PYROLYSIS FOR THE RECOVERY OF DIESEL OIL SLUDGE AND ZERO WASTE DISPOSAL

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ABSTRACT

As containing a high concentration of petroleum hydrocarbons (PHCs) and other recalcitrant components, diesel oil sludge formed in storage tanks is recognized as a hazardous waste. The management of this sludge by disposal or treatment represents a challenge with the actual economic and environmental restrictions.

A treatment process for diesel oil sludge was developed in this paper. The sludge was separated into three fractions (oil, water, and solid) where these latest are characterized, and their modes of treatment, recovery and recycling were defined. The oil fraction was treated with hot water and de-mulsifier in order to extract sodium and potassium, and their physicochemical properties were then comparable to those of the original diesel allowing its recycling. Whereas, the aqueous fraction was treated by Ferric Chloride (pH=8-9) to remove the excess of dissolved organic compounds. Their physicochemical parameters were found satisfying the permissible limits of the discharge industrial wastewater to the sea. Furthermore, catalytic thermal treatment of the solid fraction was particularly studied, and the effects of many parameters such as nature and rate of catalysts, duration and rate of heating, and temperature on the recovery of solid fraction were examined. Interesting experimental conditions were optimized as an oxygen free environment, a heating rate of 2.5 °C/min during three hours and low temperature of 300-350 °C which is the distillation range of diesel oil. A light pyro-oil and a heavy one with excellent yields (60 % and 72%) were obtained respectively with copper nitrate and sodium hydroxide as catalyst, without formation of volatile hydrocarbons. Moreover, the analysis of the obtained pyro-oil showed that is composed mainly of a mixture of aliphatic hydrocarbons chains C12-16 similarly to the composition of diesel oil. Thus, it was concluded that the solid fraction was formed by the oligomerization of those chains and the optimized operation conditions are non-destructive making their conversion to their initial structure relatively easy without being decomposed.

Globally, an appropriate Advanced Combined Technology composed of centrifuge process as the industrial process of separation and non- destructive thermal treatment process named soft pyrolysis, was defined as an efficient alternative method to the diesel sludge disposal. They are offering many benefits over other methods: valuable products, zero waste to be discharged of, achieving the environmental-friendly objectives with the most lowest cost.

INTRODUCTION

Petroleum industries generate a significant amount of oily sludge during crude oil exploration, production, transportation, storage, and refining processes [1, 2]. Oily sludge is a hazardous solid waste formed of a complex emulsion of various petroleum hydrocarbons (PHCs), asphaltenes, long chain paraffinic wax water, heavy metals, and solid particles [1, 3]. The composition of sludge varies with their origin and storage conditions [4]. It might typically contain 10-30% hydrocarbons, 5-20% solid, and 70-95% water.

Nowadays, an increasing production quantity of oily sludge has been noticed worldwide. In the USA a refinery produces annually 30 000 tons of oily sludge [5]. Around one ton of oily sludge is generated for every 500 tons of crude oil processed [6, 7], more than 1 billion tons of oily sludge has been accumulated worldwide [8, 9], and it is going to rise further in the future as the demand for petroleum product keeps on growing.

Till 2000, sludge containing more than 40% oil was known to have an elevated heating value and therefore the oil was recovered and the remaining solid was landfilled without any

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treatment. Otherwise, refineries and petroleum industries would rather accumulate this sludge in the bottom of their tanks. However, oily sludge was being recognized as a hazardous waste in many countries and causing serious threats to the receiving environment and human health [2, 10]. It contains a high level of toxic substances, can disturb the physicochemical and microbial properties of receiving soils [11], inhibits seed germination, and causes restricted growth of plants [12]. Oily sludge may migrate down through soil porosities, enters groundwater, pollutes aquatic ecosystems, and reduces diversity [13, 14]. Thus, the available options for the disposal of oily sludge have been limited and economically prohibitive. Sludge must be effectively treated and made harmless before its disposal in order to achieve the environmental-friendly objectives [15]. Traditionally, the aims of the waste processing were limited to two functions: to recover usable oil from the waste and to minimize the amount of solid waste and thus the disposal cost [16, 17, 18]. Several methods are used to separate the oil, water, and solids. The recovered oil is pumped back into the refinery process [19], while the solids and water are supposed to be treated before disposal. Several methods are available for processing and disposing of solid such as land-farming, incineration, solidification/stabilization, solvent extraction, ultrasonic treatment, pyrolysis, photo-catalysis, chemical treatment, and biodegradation [11, 16]. Each method of processing has its advantages and disadvantages. The environmental regulatory concerns have influenced and still encourage the development of more treatment and disposal options [15].

In Lebanon, The power plants and petroleum installations generate considerable amounts of sludge. Since the disposal option has gradually been narrowed, the authority has only the option of sludge storage in tanks. Currently, more than 50 000 tons are accumulated in the storage tanks of diesel oil, fuel oil, gasoline and jet fuel. The management of oily sludge becomes an acute problem due to the limitation of storage capacities and formation of clogging in filters causing companies work interruption or disturbance.

This work aimed to upgrade the operational conditions of a recovery thermal method (pyrolysis) for diesel oil sludge treatment, with respect to environmental regulations and economic requirements. Treatment procedure was divided into two steps: sludge separation and recovery of an oily fraction, and thermal conversion of the solid fraction (pyrolysis). Thus, sludge samples were collected from the tanks of the Zahrani power plant. Samples were separated into several fractions (aqueous, oil, and solid). The physicochemical properties of oily and aqueous fractions were determined and treated in order respectively to be recycled and rejected safely. Whereas the solid fraction was treated under pyrolytic conditions and the effects different operational temperatures and times were examined. Furthermore, the effect of different catalysts such as copper nitrate, sodium hydroxide, and zeolite were studied. The obtained pyro-oil and pyro-char pyro-water have been also characterized and treated for safe recycling, use and reject while pyro-gas and pyro-char were only characterized.

METHODOLOGY

Collection and filtration of diesel oil sludge sample

Sludge samples were collected from Zahrani power plant. The sampling was carried out using a glass bottle with a rope. The bottle was suspended deep in the basin where the sludge is accumulated, and drawn up gradually in order to collect the sample from all the sludge layers. Several samples with 10 L as total volume were taken and then mixed in one jerrycanin order to have a better representative sample.

Procedure of diesel sludge separation

The separation of the main components of homogeneous diesel oil sludge samples could be carried out in two steps. First, the separation of the solid phase from the liquid one was done by a simple vacuum filtration using Buchner method. Usually, at industrial scale, the separation of the solid phase from the liquid one is performed using the centrifugation method. The solid phase was then stored in containers. The second separation step corresponds to the transfer of the liquid in a separatory funnel in order to separate the oil fraction from the aqueous one. Finally, oil and water were stored in glass bottles (Figure 1). The percentages of the different separated fractions were shown in table 1. It is obvious that the percentage of each fraction depend on the sources of sludge, the conditions of storage and duration, and the cleaning frequency.

Figure1 Different fractions of diesel oil sludge: a) solid fraction, b) aqueous fraction, and c) oil fraction.

Table 1 percentages of the different components of the diesel oil sludge.

Fractions	Water	Oil	Solid
Percentage	82	6	12

Treatment procedures of Sludge fractions

Treatment of the aqueous fraction

In order to remove organic carbon from the aqueous phase (wastewater), 50 mL of water were treated with ferric chloride (dosing of $FeCl_3$) as a flocculent. Since ferric chloride is much more efficient at basic pH, the pH was adjusted to obtain a basic medium (pH 8-9) using sodium hydroxide. Samples were stirred and allowed to settle for few hours. The obtained precipitate was then removed and water became very clear.

Treatment of the Oily fraction

Oil fraction must satisfy the characteristics of the diesel oil to be used for power generation. Thus, a preliminary treatment is required in order to eliminate the sodium and potassium (together must be less than 0.3 ppm); Knowing that the presence of trace metals is harmful. In fact, sodium and potassium are more soluble in aqueous phase and then easily extracted by water. 50 mL of the separated oil was mixed with hot distilled water and a few drops of de-emulsifier. The mixture was stirred thoroughly and left 30 min for decantation. The oily phase in the upper fraction was then collected in a beaker, physicochemical analyzed, and the efficiency of the washing process was evaluated.

Treatment of the solid fraction

The thermal treatment of sludge residue was carried out at laboratory scale using a pyrolysis system. This former was built up using a 50 mL round flask as a reactor, a fractional distillation apparatus (condenser tube and a round flask for liquid collection), and a gas scrubber bottle. The conversion was performed at a relatively low temperature, normal pressure, and oxygen free environment.

Forty grams of solid sludge sample were introduced into a round flask coupled with fractional distillation apparatus. The round flask was then introduced into a controlled heater equipped with a thermocouple (Mantle Heater), and covered completely with sand in order to homogenize the heating. The heating was then initiated at a rate of 2.5 °C min^{-1} to reach the preset temperature, and remained at this temperature until complete thermal conversion (approximately 90 min). Furthermore, to obtain an inert atmosphere, nitrogen gas was injected across the system for at least 20 min while the temperature is rising till 100°C.

During the thermal conversion, the condensable phase was collected in the round flask. This phase was made of two fractions: aqueous (pyro-water) and organic (pyro-oil). These fractions were later separated using a separatory funnel and then stored in glass bottles in order to undergo the same treatment mentioned in paragraphs 2.3.1 and 2.3.2.

However, the non-condensable phase was drained in the gas cleaning system, composed of a distilled water bottle. At the end of the experiment, the system was allowed to cool down; the solid residue (pyro-char) was removed from the reactor and stored for analysis.

The effect of temperature and catalysts on the efficiency of the thermal conversion was studied. Thus several experiments were carried out at 200 °C, 250 °C, 300 °C, 350 °C, and 400°C, and 0.12 g of different catalysts were added (copper nitrate, sodium hydroxide, and zeolite).

Physicochemical analysis of sludge fractions and pyro-products

The physicochemical composition of all liquid phases generated during diesel oil sludge separation (oil and aqueous fractions) and during thermal conversion (pyro-oil and pyro-water) was studied before and after treatment. The pH and electrical conductivity were measured using Orion 4 star/Thermo scientific™ instrument. The concentrations of dissolved elements were determined by an Atomic absorption spectrophotometer (Perkin-Elmer PinAAcle 900T AAS) and ionic chromatography (Thermofisher Scientific).Dissolved anions (sulfate, nitrite, nitrate, phosphate, and chloride,…) were evaluated by spectrophotometry (Hach Spectrophotometer DR3900). The quantity of total organic carbon, total inorganic carbon, and total carbon was measured by (SHIMADZU TOC-VWS). The viscosity and the calorific value of oily phase were identified by viscometer and calorimeter, respectively. Moreover, the chemical composition of the pyro-oil was analyzed by gas chromatograph coupled with mass spectrometry (Shimadzu, GCMS-TQ8050).

Chemical analysis of the pyro-gas and the pyro-char

The chemical composition (CO, NO, NO_2, NO_X, SO_2, C_XH_Y) of the pyro-gas released during the thermal conversion was analyzed using the testo-350 portable device of the specialized laboratory of Industrial Research Institute (IRI).

Furthermore, the global calorific value, the humidity, and the sulfur content in the pyro-char were measured in the specialized laboratory of Sibline cement factory.

RESULTS AND DISCUSSIONS

Characterization and treatment of sludge fractions

The characterization of oily, aqueous and solid fractions resulting from the two separation steps of the diesel oil sludge was carried out. It is crucial to evaluate their properties and recovery methods with respect to the environmental requirements.

Oil fraction

The examination of the main parameters of the collected oily fraction is reported in the table (2). Results indicate that these parameters satisfy the limits applicable for the diesel oil used in Zahranipower plant, and that the structure has not been altered. However, a high rate of trace metals such as potassium, sodium, iron, and calcium, was reported. They are trapped in the sludge and accumulated with time.

Table 2 characteristics of the oil fraction obtained after the second separation step of the diesel oil sludge.

Parameters	Oily fraction	Limits[20]
Density at 15°c (g/cm³)	0.8532	0.82-0.876
Sulfur content (%)	0.268	< 0.3
Calorific content (MJ/Kg)	42.638	> 41.500
Aspect	Dark brown	
Viscosity (cs/cm)	4.099	1.8-5.5
Water content (%)	No water	< 0.1
Flash Point (°C)	95	> 55
Pour Point (°C)	-12	-9
Cloud Point (°C)	0	2
Miscibility with diesel oil	Yes	
Miscibility with water	No	
Sodium (ppm)	6.52	Together < 1
Potassium (ppm)	5.42	
Cadmium (ppm)	1	< 1
Iron (ppm)	1.93	< 1
Lead (ppm)	1	< 1
Calcium (ppm)	1.36	< 1
Zinc (ppm)	0.92	< 1
Ash (ppm)	No	< 100

The excess of sodium and potassium must be removed in order to make the oily fraction conform to the combustion conditions of power generation (Na + K less than 1 ppm) at Zahrani power plant. Thus, the oily fraction was treated by heated distilled water and analyzed. The efficiency of the treatment was evaluated as following:

Efficiency = [(Initial rate –Final rate)/Initial rate] * 100

The results are reported in table (3). After one treatment more than 60% of sodium and potassium were removed from the samples. Thus, the applied treatment process appears efficient. Multiple extractions will be the efficient way to reach the limit fixed at 1 ppm for sodium and potassium required limit.

Table 3 Efficiency of the treatment process.

Parameters	Beforetreatment	After treatment	Efficiency (%)	Limit
Sodium	6.52	2.45	60.80%	Together< 1
Potassium	5.43	1.84	65.92%	

Aqueous fraction

The aqueous fraction collected by decantation was yellow-brown, indicating the presence of pollutants. The examination of the values of some physicochemical parameters is reported in table (4). Results confirm the contamination expressed mainly by the high content of total organic carbon

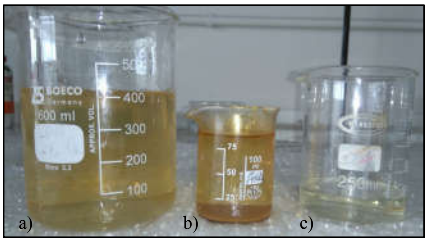

Figure 2 Aqueous fraction treated by $FeCl_3$: a) Before treatment, b) During treatment, and c) After treatment

The treatment of aqueous fraction was accomplished using a solution of ferric chloride at pH 8-9 (Figure 2). After treatment, the concentration of TOC decreased by 7.5 folds to reach 11.67 ppm (table 4). In addition, the concentrations of sodium and potassium decrease also to reach the permissible limits. The aspect of the water becomes transparent after been yellow. These results indicate clearly the efficiency of the applied treatment method, and the ability to reuse or discharge the treated aqueous fraction in the receiving environment without been toxic to aquatic life.

Table4 Analysis of aqueous fraction before and after treatment by $FeCl_3$.NA = not available

Parameters	Before Treatment	After treatment	Limits[21]
Density (g/cm³) at ˚c	1	1	1
pH at 23.8 ˚C	6.425	5.3	6-9
Conductivity (µcs/cm)at 26˚c	643	728	1000
Aspect	Yellow	Colorless	Colorless
Sodium (ppm)	525	273	NA
Potassium (ppm)	50.68	13	NA
Cadmium (ppm)	0	0	0.2
Iron (ppm)	0.38	3.6	5
Lead (ppm)	0	0	0.5
Calcium (ppm)	55.59	87.2	100
Zinc (ppm)	0.28	0.23	5
Total Carbon (ppm)	116.02	19.14	75
Total organiccarbon	89.52	11.67	NA
Total inorganiccarbon	26.5	7.47	NA
Copper (ppm)	1.13	0.4	1.5
Sulfate (ppm)	7.014	4.54	1000
Nitrate (ppm)	2.41	0	90
Nitrite (ppm)	0	0	0
Chloride (ppm)	14.28	19.83	NA
Phosphate (ppm)	3.25	2.59	5
Fluoride (ppm)	1.19	1.49	25

Solid fraction

The examination of the solid phase collected after the filtration of the diesel oil sludge looked sticky. The disposal of this fraction was the easier option, but since the recent environmental restrictions, this phase was classified as hazardous waste causing serious threats to the environment. Thus, its treatment and recovery represent a great deal to develop a complete technology to remediate all types of fuel sludge, in respect to environment conditions.

The catalytic thermal treatment of solid fraction was studied in pyrolytic conditions. The obtained products are pyro-oil, pyro-water, pyro-char and pyro-gas. The first experiments showed that the conversion could occur at a relatively low temperature under 2.5 °C/min as heating rate, for 3 hours heating, and in an oxygen-free environment. The effects of temperature and catalysts on the rate of pyro-products were followed, and the efficiency of the conversion mode was evaluated mainly by measuring the yield of pyro-oil.

Effects of temperature

Temperature is the key factor of pyrolysis, which is one of the alternative technologies for oil sludge treatment. The effects of final operating temperature (200, 250, 300, 350, and 400°C) on the thermal conversion of the solid phase were studied. Different catalysts were used such as copper nitrate, sodium hydroxide, and zeolite.

The yields of obtained pyro-products (oil-char-water) are represented in the figures (3, 5, and 7), and the evolution of pyro-oil yield (%) as versus temperature is represented in the figures (4, 6, and 8).

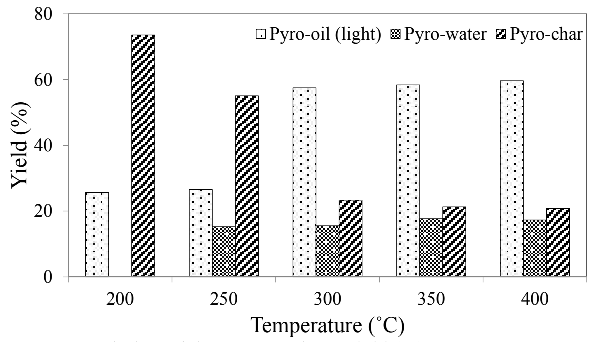

Figure 3 Evolution of the pyro-products yield (%) versus temperature. $Cu(NO_3)_2$ is used as catalyst

Figure 3 indicates that at temperature 200 °C the transformation of the solid waste starts. The yield of the pyro-oil rises with temperature to reach the maximum value (68%) at 300 °C, and it remains constant at a higher temperature. Whereas, the quantity of the pyro-char is inversely proportional to the temperature, until 300 °C, where the pyro-char yield remains constant with increasing temperature. Furthermore, the pyro-water starts forming at 250 °C and its yield (15-18 %) is not influenced by the temperature.

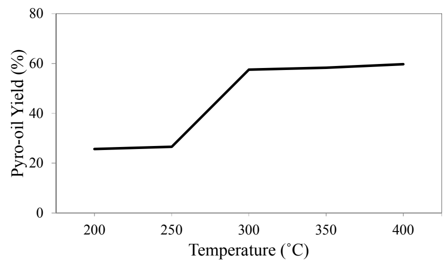

Figure 4 Variation of pyro-oil yield (%) versus temperature. $Cu(NO_3)_2$ is used as catalyst

Thus, with copper nitrate as a catalyst, 300 °C is the optimal temperature of thermal conversion under which the yield of pyro-oil is maximal and that of pyro-char is minimal (20 %).

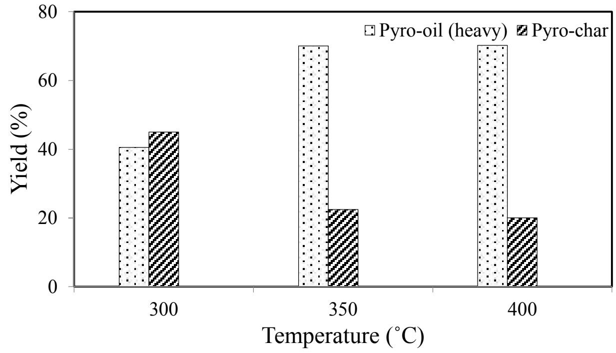

Figure 5 Evolution of the pyro-products yield (%) versus temperature. NaOH is used as catalyst

Furthermore, as sodium hydroxide is used as a catalyst, the formation of pyro-oil starts at 300 °C (Figure 5), with a yield of 40 %. The yield rises later to reach its maximum at 350 °C (72 %). The lowest yield of pyro-char (20 %) occurs at 350 °C. There is no formation of pyro-water. Nevertheless, when zeolite is added; the highest yield of pyro-oil is obtained at 400 °C (Figure 7), with a yield of pyro-char similar to those obtained with copper nitrate and sodium hydroxide.

These results reveal that the yields of the pyro-products shift from solid to liquid during the thermal conversion, with increasing temperature, whatever the added catalyst. In the presence of copper nitrate and sodium hydroxide the optimal temperature of thermal recovery ranges between 300-350 °C, which is the range of diesel oil distillation, but with zeolite the optimal conversion occurred at a temperature higher than 400 °C. Moreover, the non-formation of water with sodium hydroxide, unlike the other catalysts, may denote that water molecules are not free but weekly bonded with the components of sludge solid waste.

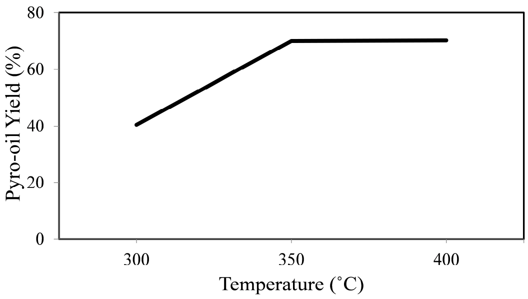

Figure 6 Variation of pyro-oil yield (%) versus temperature. Sodium hydroxideis used as catalyst

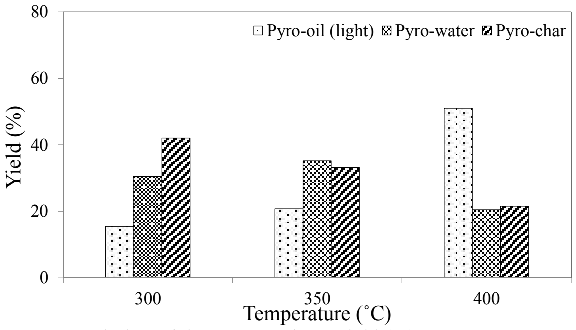

Figure 7 Evolution of the pyro-products yield (%) versus temperature. Zeolite is used as catalyst

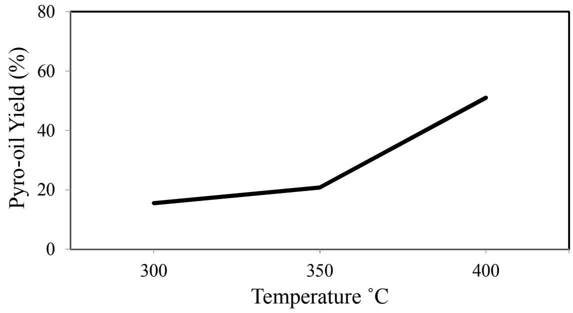

Figure 8 Variation of pyro-oil yield (%) versus temperature. Zeolite is used as catalyst

Effects of catalyst

The performance of catalysts such as copper nitrate, sodium hydroxide, and zeolite at different temperatures were studied and results are represented in figures (4-8). The comparison of their effects on the conversion rate of solid waste is represented as a function of the pyro-oil yield (%), at the optimized temperature 350 °C (Figure 9).

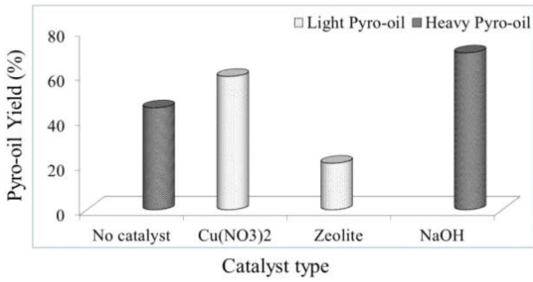

Figure 9 Variation of pyro-oil yield (%) versus type of catalyst

The comparison of the pyro-oil yields at 350 °C confirmed that the addition of catalysts to the reactor increases the efficiency of thermal treatment with different performance. In fact, yellow light oil was obtained with good yield (58 %) when the pyrolysis of the sludge solid waste was performed in the presence of copper nitrate as a catalyst. The same type of pyro-oil was obtained with zeolite as a catalyst, but with a very low yield (18 %). Thus, at 350 °C the zeolite is not efficient as catalyst for solid waste conversion, and at a temperature below 400 °C the use of zeolite is not recommended. Whereas, black heavy oil with the highest yield (72 %) was obtained when sodium hydroxide is added to the reactor as a catalyst.

Characterization and treatment of pyro-products

Pyro-water, pyro-oil, pyro-char and pyro-gas are the products of the catalytic thermal treatment of sludge solid waste at relatively low temperature (300-350 °C). The physicochemical characterization of these products was done to define their adequate use or disposal.

Pyro-water

The examination of pyro-water aspect and the results of the physicochemical analysis (table 5) showed that this pyro-product has a yellow-brown color, and contain an excessive quantity of total organic carbon (97.71 ppm). The treatment process of pyro-water was similar to that one applied to the aqueous fraction of the diesel oil sludge. It consists of the use of ferric chloride in a basic medium (pH 8 -9) (Figure 10). After treatment, the concentration of TOC decreases by 7.2

folds to reach 13.62 ppm (table 5). The aspect of water becomes transparent after been yellow. The value of pH4.6 found after treatment is due to Lewis acidity of ferric chloride. These results confirm clearly the efficiency of the applied treatment method used during the treatment of aqueous fraction. Treated pyro-water can then reused in the plant or discharged into the sea without been toxic to aquatic life

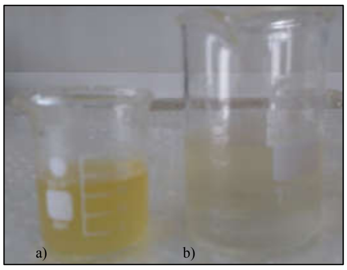

Figure 10 Pyro-water treatment by $FeCl_3$: a) Before treatment, and b) After treatment

Table 5 Physicochemical characteristics of pyro-water before and after treatment. NA = not available

Parameters	Beforetreatment	After treatment	Limits[21]
Density (g/cm³) at ˚c	1	1	1
pH at 23.8 ˚C	7.8	4.6	6-9
Conductivity(µcs/cm)at 26˚c	507	527	1000
Aspect	Yellow	Colorless	Colorless
Sodium (ppm)	514	264	NA
Potassium (ppm)	206	100	NA
Cadmium (ppm)	0	0	0.2
Iron (ppm)	0	0.34	5
Lead (ppm)	0	0	0.5
Calcium (ppm)	71	0.27	100
Zinc (ppm)	0.26	0	5
Total Carbon (ppm)	133.35	21.76	75
Total organiccarbon	97.71	12.67	NA
Total inorganiccarbon	35.64	9.09	NA
Copper (ppm)	9.7	0	1.5
Sulfate (ppm)	6	8.25	1000
Nitrate (ppm)	2.67	2.55	90
Nitrite (ppm)	0	0	NA
Chloride (ppm)	19.35	30.52	NA
Phosphate (ppm)	0	0	5
Fluoride (ppm)	0	0	25

Pyro-oil The examination of the results obtained by GC-MC (table 6) confirmed that the pyro-oil was composed mainly of aliphatic chains C12-16 that of the diesel oil.

Table 6 Chemical composition of the pyro-oil collected after catalytic thermal conversin

Peak	R.T	Intensity %	Content
1	7.994	10.7	$C_{11}H_{24}$
2	9.648	10.74	$C_{12}H_{26}$
3	11.19	16.47	$C_{15}H_{32}$
4	12.65	19.45	$C_{14}H_{30}$
5	14.01	18.39	$C_{13}H_{28}$
6	15.30	13.98	$C_{20}H_{42}$
7	16.52	10.24	$C_{21}H_{44}$

Furthermore, the physicochemical parameters of the formed pyro-oil were examined (table 7). The density, viscosity, flash point, and heating value, etc… indicate that the characteristics of the oil formed by the applied catalytic treatment at low temperature (300-350 °C) fall within the allowed range of physicochemical parameters of the original diesel oil.

Table 7 Physicochemical characteristics of the pyro-oil obtained after catalytic thermal conversion

Parameters	Pyro-oil	Limits[20]
Density at 15˚c (g/cm³)	0.8527	0.82-0.876
Sulfur content (%)	0.305	< 0.3
Calorific content (MJ/KG)	42.632	> 41.500
Aspect	Darkbrown	
Viscosity (cs/cm)	2.649	1.8-5.5
Water content (%)	0	< 0.1
Flash Point (°C)	95	>55
Pour Point (°C)	-12	-9
Cloud Point (°C)	0	2
Miscibilitywith diesel oil	Yes	
Miscibilitywith water	No	No
Sodium (ppm)	6.92	Together< 1
Potassium (ppm)	3.67	
Cadmium (ppm)	0	< 2
Iron (ppm)	3.77	< 2
Lead (ppm)	0	< 2
Calcium (ppm)	9.11	< 2
Zinc (ppm)	0.44	< 2
Ash (ppm)	42	< 100

However, as in the oily fraction extracted during diesel oil separation, analysis reports the presence of small amounts of minerals (sodium, potassium, iron, calcium,…) in the pyro-oil. Thus, in order to remove these impurities, the same procedure used to treat the oil fraction was applied. The pyro-oil was washed with distilled water and de-emulsified. The analysis of treated samples was done using AAS, and the results are reported in the table (8). Also, After one treatment more than 60% of sodium and potassium were removed from the samples. Thus, the applied treatment process appears efficient. Multiple extractions will be the efficient way to reach the limit fixed at 1 ppm for sodium and potassium required limit.

Table8 Efficiency of the treatment process.

Parameter	Beforetreatment	Aftertreatment	Efficiency	Limit
Sodium	6.92	2.34	66.2%	Together< 1
Potassium	3.67	1.11	69.7%	

Pyro-char

The analysis of the pyro-char obtained at the end of the thermal conversion (table 9) shows that pyro-char have a good Global Calorific Value (GCV = 7566 Kj/kg), an acceptable amount of ash (25 %), and a low rate of moisture (2.49 %) and sulfur (1.11 %). Thus, the analysis of pyro-char proves that this material is an energy carrier and could be used as a good fuel in cement factories for example. Moreover, the quantity of pyro-char obtained after the thermal conversion represents approximately 2.3 % of the total mass of the diesel oil sludge. Moreover, the low content of pollutants in the final solid residue makes its disposal as another safe option.

Table9 Some characteristics of the Pyro-char.

Parameters	Values
GCV (dry) (Kj/Kg)	7566
GCV (as received) (Kj/Kg)	7379
Sulfur dry (%)	1.11
Total humidity (%)	2.49
H_2O (40 °C) (%)	0.90
H_2O (100 °C) (%)	1.59
Ash dry (%)	25.79
Ash as received (%)	25.15

Pyro-gases

Usually, during the thermal conversion process, the destruction of hydrocarbon chains leads to the release of gases. Pyro-gases are the non-condensable fraction mainly composed of CO, H_2, CH_4, ect…and they are named syngas. Thus, in this study, gases released from the thermal conversion of the solid fraction were directed into a scrubber made of a distilled water bottle. These gases were analyzed and results are listed in the table (10).

Table10 Analysis of pyro-gas at the exit of pyrolysis setup. ND: not detected (detection limit 5 ppm).

Gas	Temp. (°C)	CO (ppm)	NO (ppm)	NO_2 (ppm)	NO_x (ppm)	SO_2 (ppm)	C_xH_y(ppm)
Result	33.4	422	1096	2021	3117	ND	ND

Contrarily to normal pyrolysis during thermal treatment of solid fraction, syngas was not formed. The analysis of pyro-gas listed in the table (10) indicates the absence of volatile hydrocarbons during the pyrolysis of the sludge solid fraction at low temperature 350 °C. This result confirms the conclusion found with pyro-oil, stating that the catalytic thermal treatment applied to sludge solid fraction is a non-destructive method. Furthermore, a low rate of CO was observed due to the operation under oxygen free environment. Whereas, the high rate of NO_X is related to the injection of nitrogen inside the reactor at the beginning of the pyrolysis.

CONCLUSION

Samples of diesel oil sludge were collected from Lebanese Zahrani power plant, they were separated by filtration and decantation to three fractions (oil, aqueous and solid), and, then characterized. The properties of oil fraction was found equivalent to those of original diesel. The treatment of oily fraction to remove sodium and potassium by extraction with hot water and de-mulsifier allow its safe recycling. The analysis of the brown aqueous fraction proved its contamination by dissolved organic compounds. The depollution of this fraction with ferric chloride at pH 8-9 was very efficient and treated water could be rejected safely to the sea.

Moreover, the application of catalytic thermal conversion (pyrolysis) to treat the sludge solid fraction was efficient, under specific conditions of temperature and catalysts. The optimized treatment parameters were reported as follows: (i) temperature between 300 °C and 350 °C, (ii) sodium hydroxide or copper nitrate as catalysts depending on the required type of pyro-oil (heavy or light), (iii) oxygen free environment, (iv) heating rate of 2.5 °C/min, and (v) three hours as operation time. The efficiency of the pyrolysis process was measured by evaluating the yield of the generated pyro-oil. This former was yellow and its yield was 58 % when copper nitrate was added as a catalyst, whereas, the pyro-oil was dark with 72% as yield when sodium hydroxide was the catalyst.

The formation of pyro-products (oil, water, char and gas) was reported. Pyro-oil has the same physicochemical properties of the original diesel oil, except the concentrations sodium and potassium were found in excess. Thus, pyro-oil was treated by hot water and de-emulsifier before been used as fuel and then mixed in tanks with the original diesel oil. The excess of total organic carbon in pyro-water was removed efficiently as previously by ferric chloride at pH 8-9. The analysis of the pyro-gas revealed the absence of hydrocarbon gas at the exit of the pyrolysis process. Furthermore, the pyro-char was found to be a good energy carrier, with a very low rate of pollutants.

It can be concluded that the treatment of solid fraction has occurred in relatively soft conditions. The oil was recovered at the same range of distillation temperature (300-350 °C) of the diesel oil. The easiness of thermal conversion of the solid fraction and the absence of volatile hydrocarbon let us believe that the solid sludge was composed of hydrated compounds formed of aliphatic oligomers (C12-C16) of the initial hydrocarbon chain. Thus, the process of thermal treatment was, therefore, non-destructive, and can be named **Soft Pyrolysis**.

Finally, based on experimental results and the evaluation process to achieve the environmental-friendly objectives and the most cost-effective, the followed procedure to remediate the diesel oil sludge can be defined as an **Advanced Combined Technology** (ACT). This former is composed of two steps: (i) a Centrifuge Process as the industrial process of separation, and (ii) a Soft Pyrolysis as thermal treatment process. This AEC can bedefined as a good alternative for the diesel sludge disposal. It can offer many benefits over the other methods: valuable products (diesel oil and pyro-char), zero waste to be disposed, environmental friendly technic, and low-cost treatment. The flow chart of global treatment is described in the figure (11).

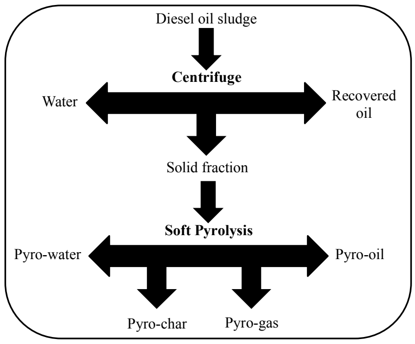

Figure 11 Flow chart of the Advanced Combined Technology (ACT).

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