Research Square

Preprints are preliminary reports that have not undergone peer review.
They should not be considered conclusive, used to inform clinical practice,
or referenced by the media as validated information.

Designing a pilot plant for treating condensed acid tar produced in oil re-refining factories as a feedstock of bitumen-based materials and catalytic cracking units

Morteza Kazemitabar
Islamic Azad University Ayatollah Amoli Branch
Mohammad reza Toosi
mrtoosi@gmail.com
Qaemshahr Branch, Islamic Azad University https://orcid.org/0000-0002-1628-7267
Shahla Fathi
Islamic Azad University Ayatollah Amoli Branch

Research Article

Keywords: Engine oil, Acid sludge, Clay, Oil refining, Acid/Clay process, Meinken Process

Posted Date: June 24th, 2026

DOI: https://doi.org/10.21203/rs.3.rs-9599932/v1

License: This work is licensed under a Creative Commons Attribution 4.0 International License.
Read Full License

Abstract

Treatment of used oil by classical acid/clay method in re-refining plants has resulted in the production of large amounts of condensed acid tar (AT), oil-saturated spent clay and liquefied wastes. In this work, an efficient pilot plant was used to separate acid compounds from the tar by designing an effective blending system for extracting acid components by increasing the area of water/oil interface. The experiments have been performed based on the factor of condensation of AT, temperature of water/oil emulsification and conducted to find the optimum conditions for the maximum efficiency of acid/tar separation. Treated tar was applied to produce bitumen-based materials after blending with rubber or convert to the hydrocarbons after thermal/catalytic cracking. Analysis of hydrocarbons after thermal/catalytic cracking showed that the distribution of types of hydrocarbons including flue gas (C_1-C_2), LPG (C_3-C_4), Naphtha (C_5-C_8), Kerosene (C_9-C_{12}), Light oil (C_{13}-C_{24}), and Heavy oil (> C_{25}) depends on the factor of tar condensation as a function of the age of condensed tar. A solvent extraction system was used to separate the residual oil in the spent clay and developed by the processes of the solvent recovery and clay regeneration with the temperature programmed oxidation (TPO). Given the successful results of pilot plant and need to provide a comprehensive waste management program, an industrial complex for simultaneous treatment of condensed AT, oil-saturated spent clay and liquefied waste was designed and calculations of energy and mass balances were carried out according to the consumption of treated sample as the requested fuel of process units.

1. Introduction

By definition, tar is known as a black semisolid mixture of heavy hydrocarbons and free carbon. It can be naturally produced by evaporation and extraction of the light hydrocarbons from the crude oil and retention of viscoelastic compounds in a natural tar pit (Daintith, 2008) or synthetically formed during destructive distillation of petroleum wastes during the recycling process of the raw materials. Spent engine oil (SEO) and other spent lubricants usually contain a gel network of soot particles (Green & Lewis, 2008; Lee & Koo, 2016) formed by partial oxidation or thermal decomposition of paraffinic/naphthenic components (Audibert 2011) and 2–6 rings polyaromatic hydrocarbons (PAH's) which are generally created by the cyclization of unburned aromatics (Fan 2010; Ogbunuzor et al., 2020). Approximately half of SEO's in industries and vehicles become waste (Moses et al., 2023) which are recycled after treatment and separation of the precipitated soot gels as condensed tar (Tasnim et al., 2025). Today, several processes such as solvent extraction (Lins et al., 2021; Nour et al., 2021; Sarkar et al., 2024), thin film evaporation (Saleem & Karim, 2020; Parekh et al., 2022), membrane filtration (Widodo et al., 2020; Rouzegari et al., 2024; Lyadov et al., 2024), and catalytic hydrotreating (Sadeek et al., 2014; Sarkar et al., 2023) have been developed for re-refining SEO alongside the old method (acid/clay) known as Minken process. The amount of discharged tar depends on the method of SEO recycling and Minken process usually produces the highest value (about 25–30 wt.% of SEO). Due to the use of sulfuric acid and polymerization/precipitation of soot particles (Ali et al., 1996, Betton 2010), about 20–25% of the tar's weight is made up of acidic compounds in form of free sulfuric acid, sulfonic acid and trapped

sulfur dioxide (Kokalj et al., 2003; Hamad et al., 2004), commonly named as acid tar (AT) or acid sludge. Since AT is classified as absolute hazardous waste by the code of 19 11 02 A for AS and 19 11 03 A (Bethel 2011), discharge of AT in the pits make serious problems for the oil re-refining plants. Meinken plants are still used in some oil-rich countries in the Middle East. There are 180 oil re-refining factories in Iran operating by use of Meinken process that deplete 75,000 tons AT annually! Unfortunately, international sanctions and the lack of attention of the international community to solve political crises have prevented the entry of advanced technologies and foreign investment for the construction of modern factories (It is necessary to prevent further environmental pollution with the possibility of transferring environmentally and friendly technologies and replacing Meinken process with them). Furthermore, the physical nature of AT depends several variables such as types of hydrocarbons (paraffinic, naphthenic, aromatic, or asphaltenes), concentration of trapped acid, and the age AT discharged into the pit. In the presence of strong acids as the catalyst, polymerization, dehydration, and polycondensation continue that causes to increase AT viscosity like the bituminous compounds (Radovanović et al., 2024). Suggestions have been made to use condensed tar as filler of bitumen-based building materials (El-Adly et al., 1997; Fakhri et al., 2021; Aliakbari et al., 2024), hot asphalt (Shishehboran et al., 2021; Liu et al., 2022) or improved green bitumen mixed by SBS rubber (Jafari et al., 2016). However, these studies did not mention how to separate acid components or neutralize AT before any application. Chlebnikovas et al. (2023) discussed the release of acidic compounds and sulfur dioxide into the air by mixing hot asphalt with the sulfur-containing rubbers. Accordingly, Radovanović et al. (2024) suggested addition of lime to neutralize AT and obtained a suitable additive for cement and pozzolanic binder. Adding lime to the condensed AT is an effective method neutralize acid compounds however, lime can increase ash content of the bitumen-based products and affect their mechanical properties. In addition, using lime-mixed tar as fuel or feedstock of oil refineries make corrosion problems because of lime salts. Extraction of the hydrocarbons by the solvent and separate them from acid components has been presented by Hadadi et al. (2019) as another method of AT treatment. Because of the use of heavy solvent (fuel oil), it seems that this process is relatively expensive due to the high energy consumption for the evaporation (310 ^{o}C) and solvent recovery.

Heavy hydrocarbons in condensed AT are potentially applicable to use as heavy fuel for ships and trains (Chihobo et al., 2016) or feed of thermal cracking and FCC units to prepare light hydrocarbons (US Department of Energy 2020). Of course, using these compounds as fuel is worth considering given the effects of fossil fuels consumption. However, using hydrocarbon wastes as fuel is better than releasing them into the environment and causing soil and water pollution (Santhoshkumar and Ramanathan, 2020). It has been proven that the rate of biological degradation of heavy hydrocarbons or decomposition by natural reagents is very slow (Some factories in Iran have depleted AT in the pit since 1980 which have remained without any change!).

It is expected that extraction of acid compounds by water alone is an effective, economic and simple method to neutralize AT. However, heavy hydrocarbons in condensed tar are highly non-polar that severely limit the penetration and diffusion of water into the organic phase. Thus, the hydrophobic nature of AT is a major challenge in the extraction of acidic compounds by use of water alone. In addition,

heating to increase water penetration into the hydrocarbon phase leads to the formation of a metastable phase system including colloidal particles of heavy hydrocarbons dispersed in aqueous phase (Raman, et al., 2016). Although there is no precise information on the nature of the interactions between acidic compounds and hydrocarbons in AT, it seems that the additives in SEO (antifoam, antioxidant, antifriction, …) act as emulsifiers and form a metastable single-phase water/oil mixture at high temperatures (Liang et al., 2016).

What could solve the problem of extracting acid from condensed tar by water is a suitable mechanism that prevents formation of water/oil emulsion and does not require the addition of lime. This allows the heavy hydrocarbons in treated tar to be used as basic material for bitumen or suitable feed for different types of heavy oils. In this work, an effective mechanical device has been designed that facilitates diffusion of water to condensed AT and successfully extracts acid compounds. In the procedure, formation of any metastable phase of the water/oil system is avoided by controlling the operating variables. After acid extraction and neutralization, production of light hydrocarbons from treated samples has been investigated using pyrolysis and catalytic cracking reactors. In addition, the remaining hydrocarbons in the condensed tar have been examined for the production of bituminous compounds.

2. Experimental

2.1. Sample preparation

Since the viscosity and density of condensed AT samples vary depending on the time of discharge, three samples were chosen: The old samples discharged more than 5 years ago, medium samples with a lifetime between 1 and 5 years, and fresh samples which have been recently discharged from the bottom effluent of distillation towers, named as S5, S1-5, and SF, respectively. S5 sample was provided by AT pits of Varian Company (Loshan City, Gilan Province) that stopped the refining SEO 5 years ago. Other samples were obtained from Avangan factory (Qorveh, Kurdistan Province) from different pits based on the time of discharge (Fig. 1a, b, and c). For each sample, six points of the pit were selected and 10 kg condensed AT was collected at each point by drilling and stored in a closed vessel made by stainless steel. Sampling was done at a depth of one meter below the tar level, where the chemical composition and physical properties do not change by environmental reagents such as sunlight and air oxygen. The samples were blended and homogenized by an electrical mixer equipped with a vertical blender shown in Fig. 1d. After 30 min, the homogenized AT was subjected to the treatment device and extract acid compounds.

2.2. Pilot plant set up

2.2.1. Acid/tar separation system

To remove acid components, a horizontal double helix blender was made by stainless steel shown in Fig. 1e. First, 60 kg AT was transferred to the blender by a feeder and 60 l water was then added to the

sample. The mixture was carefully blended by the double helix blender for 30 min. Since the first washing step involves dissolving the free acid and trapped sulfur dioxide, high concentration of acid and rising water temperature can form a metastable single-phase of water/oil, so a temperature control system and effluent discharge remove most of water-soluble organic/mineral acid compounds and prevent formation of water/oil emulsion. The wastewater was then depleted and replaced by fresh one and the mixture was blended again for next 30 min. During washing steps, the temperature was kept constant at 60°C by water jacket. The blending process was repeated until the pH of water reached up to 6. After neutralization, the wastewater was collected for the chemical analysis and further treatment. The treated sample was heated for 2 hours at 160°C and dried for the further processing.

2.2.2. Processing for the treated tar

2.2.2.1. Thermal and catalytic cracking

Thermal and catalytic cracking of treated tar was performed by means of a pyrolysis chamber in Pershianshell Company in Mahshahr Special Economic Zone (Fig. 2) developed with a catalytic cracking unit. The pyrolysis chamber was a horizontal rotary cylinder isolated by a double wall structure. The internal chamber was heated by 4 gas combustors installed in two sides of chamber and the outer wall was isolated with a layer of refractory brick. 200 kg of treated tar was fed in to the pyrolysis chamber by means of a feeder pressed with a hydraulic pump. Before heating, N_2 atmosphere was introduced for purging. The chamber was heated to 550 ^{o}C and rotated at a speed of 2 rpm. The outlet stream was imported to a cyclone to remove dust and fly ash and then fed into an isolated column with two outlets; one outlet in the top of column (for light hydrocarbons) and another outlet in the top of column (for heavy compounds). The top stream was fed into a heat exchanger to collect liquefied fractions. The gaseous outlet was compressed and collected in a cylindrical vessel. The heavy products were pumped to the catalytic cracking reactor (called riser) at a temperature range of 250–300 ^{o}C and mixed with a hot catalyst stream coming from regenerator unit. Using two hot air flows, the temperatures of riser and regenerator were adjusted at 510 and 630 ^{o}C, respectively. A commercial type of FCC catalyst (BET = 330 m^2/g, pore volume = 0.41 cm^3/g, apparent bulk density = 0.79 g/cm^3, mean particle size = 75 μm, Na_2O = 0.3%, Al_2O_3 = 42%, acidity = 401.9 μmole NH_3/g) was used for the catalytic cracking. The ratio of catalyst/oil was adjusted between 7–8. After the catalytic reactions were performed, the mixture of products and catalyst particles was entered the cyclone to separate them and the gaseous products were entered the condenser to collect liquefied and catalyst stream was injected to the regenerator to remove deposited coke and return catalyst particles to the riser.

2.2.2.2. Preparation of bitumen-like products

To modify physical and rheological properties of the condensed treated tar, sample was fed into a double layer reactor by internal volume of 20 l and equipped with an anchor agitator. The sample was mixed by the rubber of styrene-butadiene-styrene (SBS), heated to 160°C and simultaneously stirred

vigorously by the agitator. Addition of rubber was performed in the range between 1 and 5 wt.%. After cooling, the sample was characterized by conventional ASTM methods described in next section.

2.2.2.3. Extraction of residual oil

Since the main contaminant in the spent clay is the adsorbed oil during filtration step, solvent extraction was used to extract residual oil in clay. 30 kg filter cake was mixed with 300 l n-hexane and stirred for 15 minutes. The suspension was then filtered using a home-made filter press and the solution of oil/n-hexane was heated to 68 ^{o}C as the boiling point of n-hexane with a constant temperature water bath to recover the solvent. The clay was dried at 100 ^{o}C for 12 h and then heated in an electrical furnace to 700 ^{o}C with a ramp of 5 ^{o}C /min.

2.2.2.4. Wastewater treatment

The wastewater of AT treatment process was fed into to a water treatment unit containing a flocculation tank (to remove colloidal particles of soot gel), sequence absorption columns including sand, granular activated carbon (GAC), and natural zeolite (to remove residual colloids, non-burned hydrocarbons, and heavy metal ions, respectively). Analysis of water quality was performed to determine sulfuric and sulfonic acids according to the procedure reported in ASTM D4711 and the metal contents was determined by AA spectroscopy.

2.3. Samples analysis and characterization

2.3.1. Analysis of catalytic cracking products

Similar to the common cracking processes of heavy hydrocarbons and polymers (García & Juárez, 2024) it is expected that cracking of treated tar results in the production of a wide range of components that vary in terms of carbon chain length and boiling point. Based on the physical state, the products are divided to the gaseous products, liquefied fractions, and solid (coke). For better classification, a lump model for fluid catalytic cracking was used (Sani et al, 2018). The products were classified as fuel gas (C_1-C_2), LPG (C_3-C_4), naphtha (C_5-C_8), kerosene (C_9-C_{12}), light oil (C_{13}-C_{24}), heavy oil (> C_{24}), and residual solid (coke). A GC/MS chromatograph (Agilent 5975c) was used to qualitative and quantitative analysis of liquid fraction by microinjection of the sample to the GC device equipped with a capillary column (l = 30 m, type DB-2887) The gaseous components were directly fed in to GC/MS instrument using an automatic gas sampler. Mass balance calculations was applied to estimate yield of the products (wt.%) according to the conversion of the feed to the gaseous, liquefied, and solid (coke) products.

The yield of products was observed as the mole number of C atoms:

Yield = $x_i n_i / \Sigma x_i n_i$

where x_i a n_i are the fraction and the number of carbon atoms of the product *i*.

2.3.2. Characterization of the treated tar and bitumen

A common set of ASTM methods were used to determine mechanical, physical, and chemical properties of the treated tar basically applied for the bitumen-based materials. These methods contain penetration degree (Penetration Needle ASTM D5), specific gravity (Pycnometer method ASTM D70), softening point (ring-and-ball apparatus ASTM D36), kinematic viscosity (ASTM D2170) and ductility (ASTM D113). In addition, the neutralized tar was analyzed to measure the amount of sulfur, ash content (ASTM D8078), and solubility in CS_2 (ASTM D4).

2.3.3. Analysis of the recovered oil and clay

Thermal behavior of the spent clay was characterized by TGA analysis and estimated oil content, weight loss (LOI), and the ash content were determined. Moreover, DTA diagram was provided to obtain a temperature range for the evaporation of residual oil and combustion of soot gel in the clay. The treated sample was also characterized by XRF measurement and compared with the fresh bentonite. In addition, BET measurement was used to determine pore volume and surface area of bentonite after thermal treatment.

A series of common ASTM tests were used to analyze the oil samples obtained from the spent clay. The test method for ASTM color of the oil sample was done by ASTM D1500. Other parameters and their ASTM numbers were density (D1298), viscosity (D445), total acid number (D974), flash point (D92), and pour point (D97). Elemental analysis was performed by atomic emission spectroscopy (Agilent 4210 MP-AES) (D8322).

3. Results and discussion

3.1. Characterization of the treated tar

3.1.1. Chemical analysis

Analysis of SIMDIS-GC data for C-atom distribution of the treated sample is shown in figure 3. It is observed that SF sample contains 3.5 wt.% of gasoline fraction (C_5-C_{10}), 46.5 wt.% of diesel fraction (C_{11}-C_{22}), and 50 wt.% of heavy fraction (>C_{22}). It is also observed that the carbon atom distributions for S1-5 and S5 samples (based on above classification) are: 2.3, 34.4, 63.3 and 1, 19.3, and 79.7 wt.%, respectively. It can be seen that the distribution of carbon atoms for heavy fractions increases with the age of tar in the pit. This observation can be explained by evaporation of light fractions by sunlight and polycondensation of functionalized chains in the presence of acidic compounds as catalysts (Cukier, et al., 1988). This confirms that the accumulation of acidic tar for a long time causes it to harden and makes the process of discharge and transport it more difficult which increases both the harmful environmental pollution and cost of transportation.

Details of acidity of the wastewaters show that while the acid concentration is more than 1 M in the first washing step, the concentration decreases to 6.44×10^{-7} M (pH=6.191), 4.9×10^{-6} M (pH=5.310), and 3.01×10^{-6} M (pH=5.51) after 3th step for SF, S1-5, and S5, respectively. Analysis of spent water for SF

sample shows that 89 wt.% of dissolved acids is sulfuric acid and others contain sulfonic derivatives such as methane sulfonic acid or other linear samples. These values for S1-5 and S5 are 73 and 52 wt.%, respectively. It means that the amounts of sulfonic acid derivatives increase with time and the amount of sulfuric acid decreases. Elemental analysis shows that the amounts of Co^{+2}, Fe^{+2}, Ni^{+2}, Pb^{+2}, and Cr^{+3} in wastewater of SF treatment are 24, 159, 123, 18, and 57 ppm, respectively. It is also observed that using ammonium sulfide, the amounts of these metal ions decrease to 1, 11, 84, 7, and 2 ppm, respectively.

3.1.2. Physical and mechanical properties

The physical and chemical characteristics of the tar samples before and after treatment are shown in Table 1. To compare these properties with a standard sample, bitumen 60/70 was used as a common reference in bitumen products (zakaria, et. al., 2018). The details indicate that there is a good similarity in several properties between the treated samples and standard sample. The softening points of samples SF, S1-5, and S5 are 53, 56, and 58 ^{o}C, respectively. They are in the range of the reported values for bitumen 60/70 (46-56 ^{o}C). Values of kinematic viscosity for SF, S1-5, and S5 samples are 243, 242, and 248 cSt., respectively (close to the value of the standard sample i.e. 240 cSt). Furthermore, other properties, including specific gravity, solubility (in CS_2) and ash content for three samples are close to the standard value. It can be seen that the treated samples are good candidate for use in bitumen-based products. However, details show some differences between the treated tars and standard value e.g. penetration and ductility. While the range of penetration in standard bitumen is 60-70 (in 0.1 mm), the values for SF, S1-5, and S5 samples are 43, 25, and 21 (in 0.1 mm), respectively. In addition, ductility of standard bitumen is at least 100 cm but the values of ductility for SF, S1-5, and S5 are 25, 21, and 20 cm, respectively.

3.2. Analysis of the products

3.2.1. Catalytic cracking products

The details of the cracking experiments are given in Table 2. The results show that the amounts of gaseous and liquefied products in the presence of catalyst are higher than those in the experiments without catalyst. While the residual coke amounts without catalyst for samples SF, S1-5 and S5 are 3.9, 16.3 and 16.9 wt.%, these values are 0.3, 2.3 and 2.6 wt.% by catalyst, respectively. In addition, the amount of heavy oil ($>C_{24}$) is higher than the other derivatives in the experiments without catalyst, while the highest amount of the products is related to light oil (C_{13}-C_{24}) in the presence of catalyst. The results also show that SF sample produces more liquid products and less coke than S1-5 and S5 samples. Comparison of the amount and distribution of products from catalytic and thermal cracking of neutralized tar with those from plastic and used tire cracking shows a similar mechanism in catalytic and thermal cracking. Certainly, the mechanism of thermal and catalytic cracking reactions can never be fully understood due to the high temperatures, the variety of feedstock's, the large number of intermediates, and the complex reaction networks. Different mechanisms have been proposed for

different plastic wastes, the type of catalytic process, and the type of catalyst used. One of the most important mechanisms proposed for zeolite catalysts is the carbenium intermediate (Corma and Orchilles 2000). This mechanism has been proposed as the formation of a carbenium ion as a result of protonation on Brønsted sites and hydride abstraction on Lewis sites. The carbenium mechanism includes initiation steps during protonation or hydride decomposition, dipropagation through chain breakage on the active sites of the catalyst, and isomerization or aromatization of the carbenium species. Other mechanisms have been also proposed for catalytic mechanisms for in-situ and ex-situ systems. For example, a radical mechanism involving initiation, formation of second-order radicals, and termination via proton transfer has been proposed (Saha et al., 2024).

3.2.2. Rubber-mixed products

Table 3 shows the characteristics of modified treated samples after mixing with SBS in different contents. The results show that the ductility of the treated samples increases significantly with the addition of rubber. For SF samples, the addition of 5 wt.% rubber increases the ductility from 25 to 102 cm. For S1-2 and S5 samples, the ductility increases from 21 and 20 cm to 65 and 66 cm, respectively. Furthermore, by adding 5 wt.% rubber to SF, S1-5 and S5 samples, the kinematic viscosity increases from 203, 212 and 218 cSt to 247, 249 and 252 cSt, respectively. It is explained that the addition of rubber increases intermolecular interactions and creates more cross-links in the matrix composition. The increase in the softening point in samples containing rubber compared to the original samples can be another evidence of this claim. Enhancement of the physical/mechanical properties of treated samples by optimizing the amount of rubber can provide the desired conditions for their application in the road construction, civil engineering and insulation products.

3.2.3. Liquefied products

Analysis of the oil samples from treated SF and the spent clay is given in table 4. (It should be notified that fresh AT includes residual oil which can be easily recycled after deposition of condensed part of AT while S15 or S5 samples do not contain any liquefied part). It is observed that the use of hexane solvent instead of DME (Zhang et al., 2021) shows more efficiency in extracting oil from the clay. It seems that non-polar nature of hexane enhances the dissolution of oil hydrocarbons more than DME and performs better efficiency in extracting oil from the spent clay. Results of gravimetric analysis for the spent clay and recovered oil (Figures 4a and b) show that about 20 wt.% of the oil is adsorbed by the clay. Given the large amount of clay consumed in the acid/clay method (an average of 10 tons per day), the adsorption of oil on the clay not only reduces the efficiency of the acid/clay process but also adds to the environmental problems of this method (These are other reasons to replace the old method with modern plants). The results regarding the total acid number (TAN) show that both the recovered oil from the spent clay has low acidity and treated SF sample are reported in accordance with the standard value (Salem et al., 2015).

3.2.4. Treated clay

Details of analysis of bentonite after oil extraction and thermal treatment are given in table 5. Comparison of the weight percentages of the mineral oxide in the regenerated bentonite with the fresh one shows that the chemical composition of bentonite remains unchanged during the regeneration process. Results also show that the weight loss of ignition (LOI) at 1000 ^{o}C in the treated clay is almost equal to the fresh sample. Details of BET measurements for the regenerated and fresh clays in table 5 indicate that the thermal treatment leads to a decrease in surface area of bentonite from 31.8 to 27.7 m^2/g. Also, the pore volume and average pore diameter decrease from 0.093 to 0.082 cm^3/g and 11.7 to 12.2 nm, respectively. It can be concluded that thermal treatment up to 500 ^{o}C successfully removes impurities such as PAH's and gel particles deposited on the clay (Figures 4c and d) and the decrease in surface area and pore volume in bentonite is due to the blockage of pores by thermal treatment (sintering), not caused by coke deposition (fouling) in the pores.

Figure 5 shows TGA/DTA plot of the spent clay. Two main peaks correspond to the weight losses due to the volatilization of adsorbed oil and soot gel burning. The first peak is observed in the range of 190-360 °C with the weight loss of 23 wt.%. It is seen that the amount of weight loss corresponds to the amount of oil recovered by the method of solvent extraction. The second weight loss in the temperature range of 390 to 585 °C is approximately 14%. Considering the release of soot and coke deposited on the clay up to 600 °C, it can be expected that calcining spent clay up to this temperature is a suitable method for clay regeneration for reuse or any other application without environmental pollution.

3.3. Engineering and economic aspects

3.3.1. Design of treatment plants

Considering the requirements of acid/clay plants to comprehensively manage hazardous wastes, designing a complex plant of treatment units can solve serious environmental problems. The obtained results of pilot scale for designing a continuous large plant are as follows:

1. Repeated washing method with a special mixing system can neutralize AT by water alone. Acidic wastewater can be reused after precipitation of metal ions and neutralization

2. Adding rubber to neutralized tar improves mechanical properties of bitumen-based materials.

3. n-Hexane can effectively extract oil from the spent clay in acid/clay plants and reused after evaporation. Calcination of spent clay removes the impurities and regenerates for reusing.

4- Given the successful neutralization of the tar, it can be used as the fuel and thermal pyrolysis of tar provides heavy oil similar to the recovered oil extracted from spent clay.

6. Catalytic cracking of tar produces liquid derivatives suitable for using as light fuel.

Figure 6 shows PFD diagram of a continuous plant for AT treatment. In unit #1, AT is fed into an extruder through a feeder, homogenized and simultaneously washed with water. The feed is then injected to a

double helix mixer and washed with hot water at 60 ^{O}C. Both the extruder and the helix mixer are designed to facilitate water penetration into the condensed tar for better extraction of acid. The washing cycles are repeated until the pH of the solution reaches the neutral range. After it, the treated AT is pumped to the blending tank and mixed with SBS in unit #2. In third unit, the treated AT is fed into a pyrolysis chamber and fluid catalytic cracking (FCC) unit. FCC process generally contains a riser as catalytic cracking reactor and reactor of catalyst regeneration (regenerator). The acidic effluent passes through an adsorption column containing silica or activated alumina after precipitation of metal ions and neutralization in unit #4. The solution is then injected to the evaporator and water returns to AT treatment cycle. In unit #5, the spent clay is mixed with n-hexane and the slurry mixture is transferred to the filter press to separate the oil/clay suspension. The solution is then fed into the boiler and heated up to 68 ^{O}C to extract the solvent and recover after condensation. Finally, the filter cake is dried in a dryer and then calcined in a rotary kiln.

3.3.2. Material and energy balances

The calorimetric results show that the heat of combustion of treated tar is about 41.3 kJ. Like petroleum bitumen, heavy hydrocarbons and PAH's increase the heat of combustion of tar so, it can be used as fuel for energy source after cracking. According to PFD diagram of treatment plant, a dryer, a pyrolysis chamber, a catalyst reactor (riser), regenerator, a rotary kiln (clay regenerator), and a boiler (solvent recovery unit) are the equipments that consume energy as heat. The mass and energy balance calculations have been carried out with Engineering Equation solver (EES v.10.561) and the results are shown as a snaky diagram in figure 7. According to the water percentage of treated tar (11 wt.%), 232.45 kJ heat needs to dry the treated sludge which is equal to complete burn of 0.006 kg dried treated sludge. Considering need of hot air stream for pyrolysis chamber (550 ^{O}C), regenerator (630 ^{O}C), riser (510 ^{O}C), and clay regenerator (550 ^{O}C), the energy consumption for these processes are 553.4, 633.9, 513.2, and 553.4 kJ, respectively. The total consumption of treated tar for the above devices is 0.055 kg. Based on the experiments, 10 l hexane is needed for oil extraction from 1 kg spent clay. Considering the heat of vaporization of hexane (28.85 kJ/mol), 2209.496 kJ heat is needed to evaporate and recover hexane, equivalent to 0.054 kg of neutralized tar. The amount of heat required to dry 1 kg treated tar (based on 14 wt.% moisture) is 230 kJ (0.006 kg of dry tar). Considering energy loss in above processes as 10 %, it is seen that 13.2 % of treated AT is consumed as fuel in treatment units; 25% is extracted as water-soluble acid compounds and 61.8% is available for the production of bitumen-based materials or thermal/catalytic cracked hydrocarbons.

4. Conclusion

Our experiments have shown that the extraction of acid compounds from condensed acid tar of re-refining plants can be successfully done by means of an efficient washing system equipped with a double helix blender that increases the area of oil/water interface. Prevention of metastable oil/water single phase can be achieved by controlling the temperature of the mixture below 60 ^{O}C, slight acid

extraction and decrease of acid concentration step by step. Solvent extraction method by n-hexane can efficiently separate residual oil from the oil-saturated spent clay as another harmful waste of acid/clay plants. The spent clay can be successfully reused after regeneration by TPO process. Thermal pyrolysis of three types of treated tar produces a wide range of hydrocarbons containing flue gas (1-1.1%), LPG (2.7-3%), naphtha (4.1–5.7%), kerosene (13.8–14.5%), light oil (21.5–26%), heavy oil (40-45.8%), and coke (3.9–16.9%). Catalytic cracking produces more light products than thermal pyrolysis (93.9–96.8%). It has been found that the old tar sample (S5) produces heavier fractions and residual coke more than the fresh sample (SF), which alone has 20 wt.% of the extractable liquid oil.

A large scale unit was designed for the simultaneous treatment of condensed AT, the spent clay and wastewater treatment, noting that all the heat required for the catalytic cracking, evaporator, and dryer, would be provided by using neutralized tar. Material and energy balance calculation showed that 13.2% of treated AT is consumed as fuel in the units of pyrolysis, FCC reactor, clay regenerator, and solvent evaporator; 25%wt. of AT contains water-soluble acid compounds and 61.8% can be used for the production of bitumen-based materials or hydrocarbon fuel after thermal/catalytic cracking.

Declarations

Acknowledgment

This work was supported by Ayatollah Amoli Branch of Islamic Azad University (IAU) and authors would like to thank the CEO of Pershianshell for his cooperation in providing the pyrolysis unit.

Author contribution

All authors contributed to the study conception and design. Sample collection was performed by MK. Analyses were performed by MK and SF. Result discussion and manuscript preparation were performed by FK and MRT. All authors read and approved the final manuscript.

Funding: This study did not receive any funding.

Ethical approval Not applicable.

Consent to participate Not applicable.

Consent for publication

All authors have read and approved the final version of the manuscript and consent to its publication.

Competing interests

The authors declare that they have no competing interests.

Data availability

All data generated or analyzed during this study are included in this published article and its supplementary information files.

References

1. Ali, M.F., Rahman, F. and Hamdan, A.J., 1996. Techno-economic evaluation of waste lube oil rerefining. International journal of production economics, 42(3), pp.263-273. https://doi.org/10.1016/0925-5273(95)00176-X
2. Aliakbari, A., Hajikarimi, P. and Khodaii, A., 2024. The effect of eco-friendly functionalised acid sludge on thermo-rheological characteristics of bituminous composites. Road Materials and Pavement Design, pp.1-21. https://doi.org/10.1080/14680629.2024.2324962
3. Audibert, F., 2011. Waste engine oils: rerefining and energy recovery. Elsevier. PP 10-11.
4. Bethel, N., 2011. Environment Agency Hazardous Waste: Interpretation of the definition and classification of hazardous waste. https://www.gov.uk/government/organisations/environment-agency
5. Betton, C.I., 2010. Lubricants and their environmental impact. Chemistry and technology of lubricants, pp.435-457. https://doi.org/10.1023/b105569_15
6. Chihobo, C.H., Chowdhury, A., Kuipa, P.K. and Simbi, D.J., 2016. Pyrolysis characteristics and kinetics of acid tar waste from crude benzol refining: A thermogravimetry–mass spectrometry analysis. Waste management & research, 34(12), pp.1258-1267. https://doi.org/10.1177/0734242X16669999
7. Chlebnikovas, A., Marčiulaitienė, E., Šernas, O., Škulteckė, J. and Januševičius, T., 2023. Research on air pollutants and odour emissions from paving hot-mix asphalt with end-of-life tyre rubber. Environment International, 181, p.108281. https://doi.org/10.1016/j.envint.2023.108281
8. Corma A., Orchilles AV., 2000. Current views on the mechanism of catalytic cracking. Micropor Mesopor Mater 36, 21-30, https://doi.org/10.1016/s0167-2991(08)61903-5
9. Cukier S., Camp M. D., (1988) Polycondensates of sulfonated coal tar fractions, US patent No 4744882A
10. Daintith, John (2008). "tar". A Dictionary of Chemistry (6th ed.). Oxford University Press. doi:10.1093/acref/9780199204632.001.0001
11. El-Adly, R.A., Moustafa, Y.M. and Omar, A.M.A., 1997. Gilsonite varnish from acid sludge produced by the recovery of used lubricating oil. Pigment & resin technology, 26(4), pp.221-224. https://doi.org/10.1108/03699429710174116
12. Fakhri, M., Arzjani, D., Ayar, P., Mottaghi, M. and Arzjani, N., 2021. Performance Evaluation of WMA Containing Re-Refined Acidic Sludge and Amorphous Poly Alpha Olefin (APAO). Sustainability, 13(6), p.3315. https://doi.org/10.3390/su13063315
13. Fan, W.T.C., 2010. Regeneration of used petroleum-based lubricants and biolubricants by a novel green and sustainable technology (Doctoral dissertation, University of Southern California).

14. García, F. D. J. O., & Juárez, E. M. (2024). Polyethylene waste co-processing in fluid catalytic cracking plants. Cleaner Engineering and Technology, 19, 100734. https://doi.org/10.1016/j.clet.2024.100734
15. Green, D.A. and Lewis, R., 2008. The effects of soot-contaminated engine oil on wear and friction: a review. Proceedings of the Institution of Mechanical Engineers, Part D: Journal of Automobile Engineering, 222(9), pp.1669-1689. https://doi.org/10.1243/09544070JAUTO468
16. Hadadi, V. and Moradi, A., 2019. A novel method for refining of acidic sludge and mixing with vacuum bottom to improve bitumen properties. Petroleum Science and Technology, 37(13), pp.1529-1538. https://doi.org/10.1080/10916466.2019.1573258
17. Hamad, A., Al-Zubaidy, E. and Fayed, M.E., 2004. Assessment of used motor oil recycling opportunities in the United Arab Emirates. Journal of King Saud University-Engineering Sciences, 16(2), pp.215-227. https://doi.org/10.1016/S1018-3639(18)30788-8
18. Jafari, A.J., Hassanpour, M. and Farzadkia, M., 2016. Economic evaluation of recycling acidic sludge project of reprocessing industries to bitumen (A case study). Environmental technology & innovation, 5, pp.30-40. https://doi.org/10.1016/j.eti.2015.11.004
19. Kokalj, F., Samec, N. and Perdija, B., 2003. ENVIRONMENTALLY SAFE REMEDIAL OF ACID SLUDGE BY INCINERATION. Goriva i Maziva, 42(4), p.251. https://hrcak.srce.hr/clanak/11106
20. Lee, H. and Koo, S., 2016. Analysis of fractal aggregates in a colloidal suspension of carbon black from its sedimentation and viscosity behavior. Korea-Australia Rheology Journal, 28, pp.267-273. https://doi.org/10.1007/s13367-016-0028-1
21. Liang, C., Liu, Q. and Xu, Z., 2016. Dewatering Bitumen emulsions using interfacially active organic composite absorbent particles. Energy & Fuels, 30(7), pp.5253-5258. https://doi.org/10.1021/acs.energyfuels.6b00228
22. Lins, T.S., Pisoler, G., Druzian, G.T., Negris, L., Decote, P.A., Vicente, M.A., Flores, E.M. and Santos, M.F., 2021. Base oil recovery from waste lubricant oil by polar solvent extraction intensified by ultrasound. Environmental Science and Pollution Research, 28(46), pp.66000-66011. https://doi.org/10.1007/s11356-021-15582-y
23. Liu, Q., Han, B., Wang, S., Falchetto, A.C., Wang, D., Yu, B. and Zhang, J., 2022. Evaluation and molecular interaction of asphalt modified by rubber particles and used engine oil. Journal of Cleaner Production, 375, p.134222. https://doi.org/10.1016/j.jclepro.2022.134222
24. Lyadov, A.S., Kochubeev, A.A. and Nebesskaya, A.P., 2024. Regeneration of Waste Motor Oils Using Membranes (a Review). Petroleum Chemistry, pp.1-9. https://doi.org/10.1134/S0965544124080139
25. Moses, K.K., Aliyu, A., Hamza, A. and Mohammed-Dabo, I.A., 2023. Recycling of waste lubricating oil: A review of the recycling technologies with a focus on catalytic cracking, techno-economic and life cycle assessments. Journal of Environmental Chemical Engineering, 11(6), p.111273. https://doi.org/10.1016/j.jece.2023.111273
26. Nour, A.H., Elamin, E.O., Nour, A.H. and Alara, O.R., 2021. Dataset on the recycling of used engine oil through solvent extraction. Chemical Data Collections, 31, p.100598. https://doi.org/10.1016/j.cdc.2020.100598

27. Ogbunuzor, C.C., Hellier, P.R., Talibi, M. and Ladommatos, N., 2020. In-cylinder polycyclic aromatic hydrocarbons sampled during diesel engine combustion. Environmental Science & Technology, 55(1), pp.571-580. https://doi.org/10.1021/acs.est.0c05561
28. Parekh, K., Gaur, R. and Shahabuddin, S., 2022. Recent advances in reclamation of used lubricant oil. Tailored Functional Materials: Select Proceedings of MMETFP 2021, pp.273-282. https://doi.org/10.1007/978-981-19-2572-6_21
29. Radovanović, D., Štulović, M., Ranitović, M., Djokić, J., Andjić, Z. and Kamberović, Ž., 2024. Acid tar treatment—the transformation of organic waste into “organic core—inorganic shell” structure particles. Journal of Material Cycles and Waste Management, 26(5), pp.2947-2960. https://doi.org/10.1007/s10163-024-02012-7
30. Raman, A. K. Y., Venkataramani, D., Bhagwat, S., Martin, T., Clark, P. E., & Aichele, C. P. (2016). Emulsion stability of surfactant and solid stabilized water-in-oil emulsions after hydrate formation and dissociation. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 506, 607-621. https://doi.org/10.1016/j.colsurfa.2016.06.042
31. Rouzegari, F., Sargolzaei, J. and Ramezanian, N., 2024. A composite ultrafiltration membrane for regeneration of used engine oil. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 46(1), pp.16897-16912. https://doi.org/10.1080/15567036.2020.1818009
32. Sadeek, S.A., Ahmed, H.S., ElShamy, E.A., El Sayed, H.A. and Abd El Rahman, A.A., 2014. Hydrotreating of waste lube oil by rejuvenated spent hydrotreating catalyst. Egyptian Journal of Petroleum, 23(1), pp.53-60. https://doi.org/10.1016/j.ejpe.2014.02.008
33. Saha, B., Vedachalam, S., Dalai, A. K., Saxena, S., Dally, B., Roberts, W. L., 2024, Review on production of liquid fuel from plastic wastes through thermal and catalytic degradation, 114, 101661. https://doi.org/10.1016/j.joei.2024.101661
34. Saleem, H.J. and Karim, A.R., 2020. Re-refining of used lubricating oil by vacuum distillation/thin wiped film evaporation technique. Petroleum Science and Technology, 38(4), pp.323-330. https://doi.org/10.1080/10916466.2019.1704782
35. Salem, S., Salem, A. and Babaei, A.A., 2015. Preparation and characterization of nano porous bentonite for regeneration of semi-treated waste engine oil: Applied aspects for enhanced recovery. Chemical engineering journal, 260, pp.368-376. https://doi.org/10.1016/j.cej.2014.09.009
36. Sani, A. G., Ebrahim, H. A., & Azarhoosh, M. J. (2018). 8-Lump kinetic model for fluid catalytic cracking with olefin detailed distribution study. Fuel, 225, 322-335. https://doi.org/10.1016/j.fuel.2018.03.087
37. Santhoshkumar, A. and Ramanathan, A., 2020. Recycling of waste engine oil through pyrolysis process for the production of diesel like fuel and its uses in diesel engine. Energy, 197, p.117240. https://doi.org/10.1016/j.energy.2020.117240
38. Sarkar, S., Datta, D., Deepak, K.S., Mondal, B.K. and Das, B., 2023. Comprehensive investigation of various re-refining technologies of used lubricating oil: a review. Journal of Material Cycles and Waste Management, 25(4), pp.1935-1965. https://doi.org/10.1007/s10163-023-01685-w

39. Sarkar, S., Datta, D. and Das, B., 2024. Experimental elucidation of performance of four extracting solvents for reclamation of spent lubricating oil using extraction–flocculation process. Clean Technologies and Environmental Policy, pp.1-19. https://doi.org/10.1007/s10098-024-02856-5
40. Shishehboran, M., Ziari, H., Korayem, A.H. and Hajiloo, M., 2021. Environmental and mechanical impacts of waste incinerated acidic sludge ash as filler in hot mix asphalt. Case Studies in Construction Materials, 14, p.e00504. https://doi.org/10.1016/j.cscm.2021.e00504
41. Tasnim, A., Abha, A.T., Naghibalsadati, F., Tam, E. and Ng, K.T.W., 2025. Management Assessment of used Oil, Filters, and containers in the Canadian automotive sector using resource recovery metrics. Waste Management, 191, pp.284-293. https://doi.org/10.1016/j.wasman.2024.11.020
42. US Department of Energy (2020) Used Oil Management and Beneficial Reuse Options to Address Section 1: Energy Savings from Lubricating Oil Public Law 115-345, p 124
43. Widodo, S., Khoiruddin, K., Ariono, D., Subagjo, S. and Wenten, I.G., 2020. Re-refining of waste engine oil using ultrafiltration membrane. Journal of Environmental Chemical Engineering, 8(3), p.103789. https://doi.org/10.1016/j.jece.2020.103789
44. Zakaria, N.M., Hassan, M.K., Ibrahim, A.N.H., Rosyidi, S.A.P., Yusoff, N.I.M., Mohamed, A.A. and Hassan, N., 2018. The use of mixed waste recycled plastic and glass as an aggregate replacement in asphalt mixtures. Jurnal Teknologi, 80(1). https://doi.org/10.11113/jt.v80.11147
45. Zhang, D., Huang, Y., Oshita, K., Takaoka, M., Wang, Q., Sheng, C. and Lin, Z., 2021. Liquefied dimethyl ether based multi-stage extraction for high efficient oil recovery from spent bleaching clay. Waste Management, 136, pp.204-212. https://doi.org/10.1016/j.wasman.2021.09.033

Tables

Tables 1 to 5 are available in the Supplementary Files section.

Figures

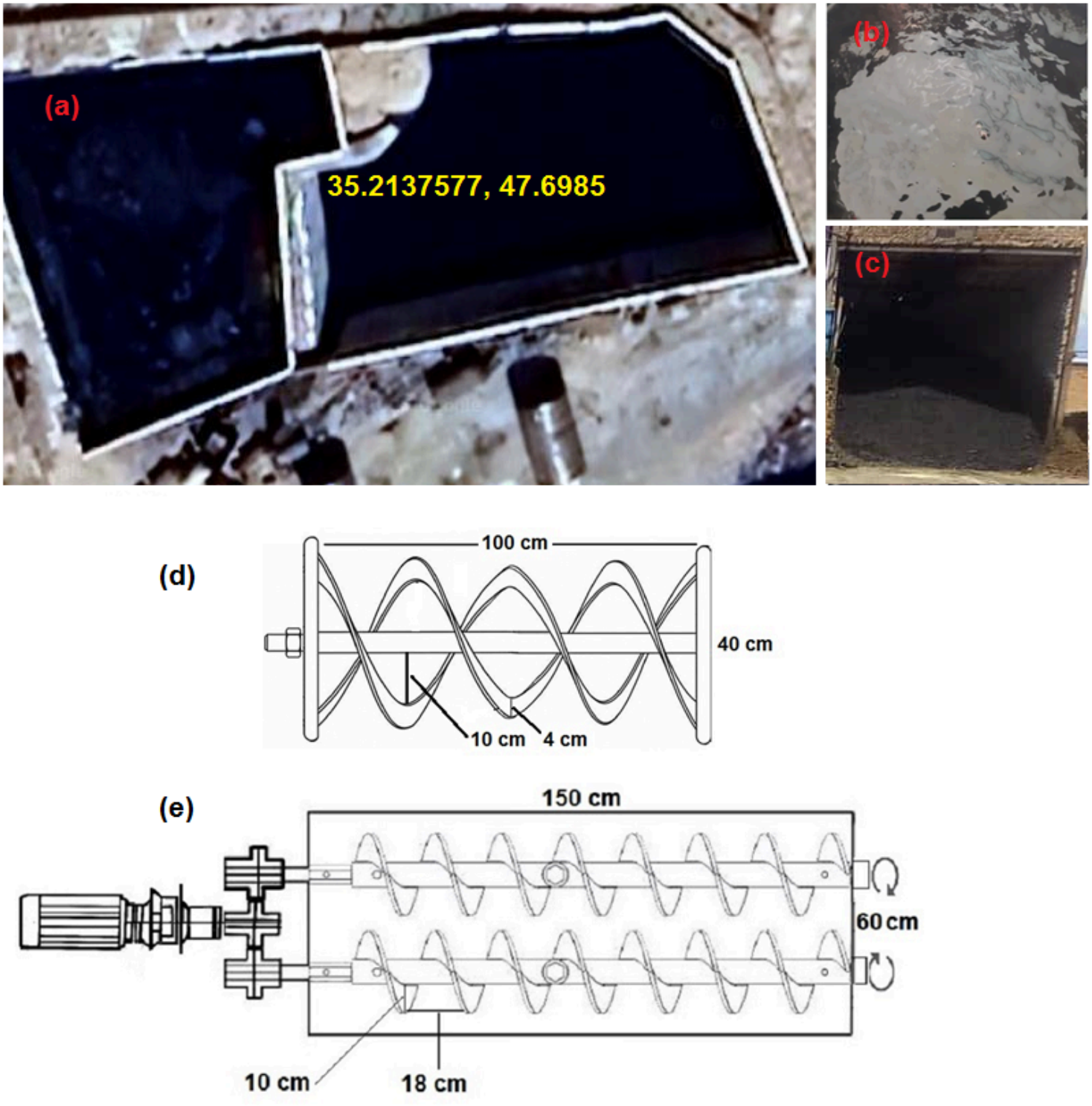


Figure 1

(a) a location of AT pet in Kurdistan Province (b) Liquefied waste (c) spent clay storage (d) condensed tar blender (e) Double helix blender



Figure 2

Different parts of pyrolysis reactor; (a) reactor inlet, (b) rotary system, (c) cyclone, (d) condenser, (e) liquids storage, (f) gas container

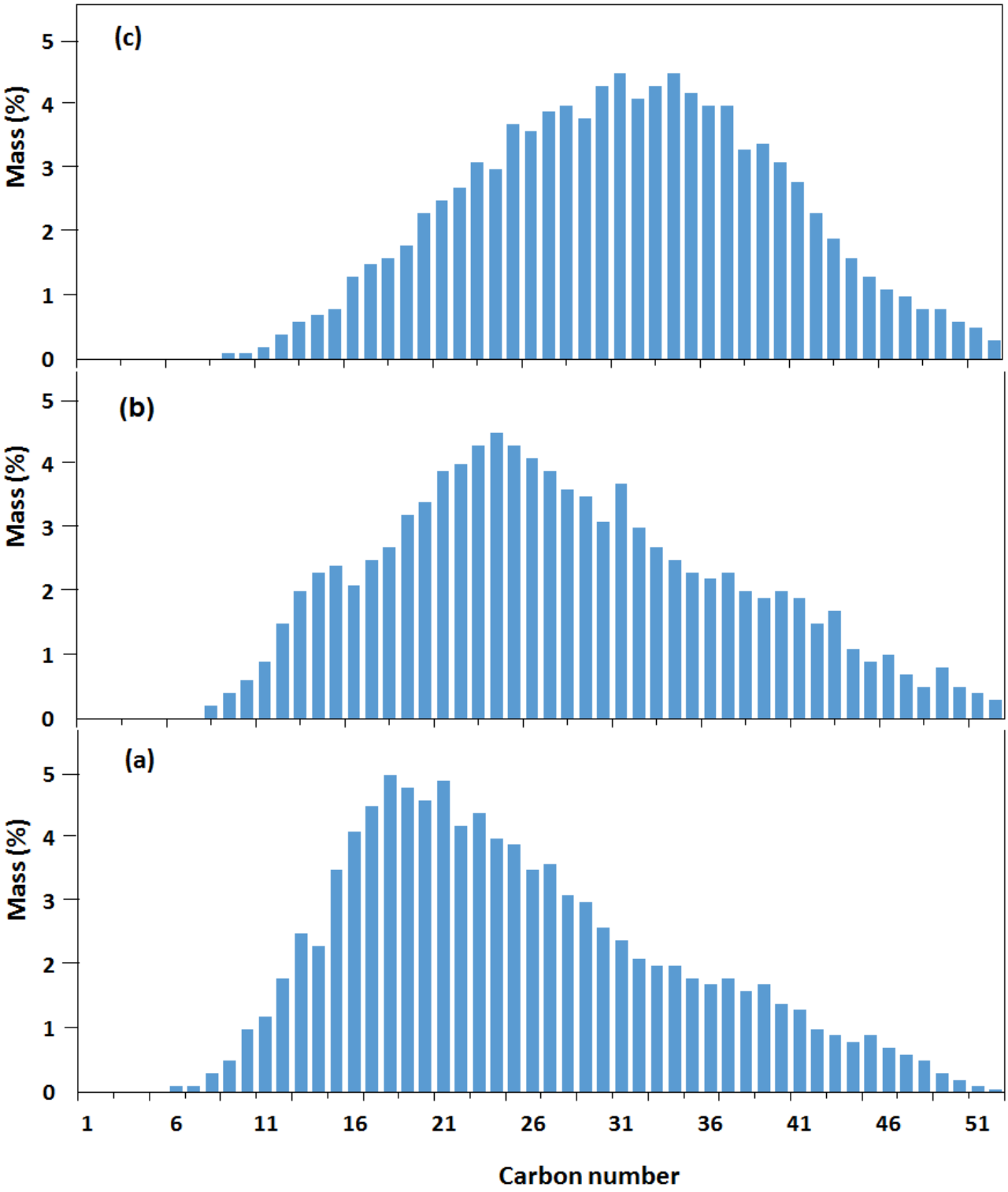


Figure 3

Analysis of SIMDIS-GC data for C-atom distribution of the treated samples SF (a), S15 (b), and S5 (c)

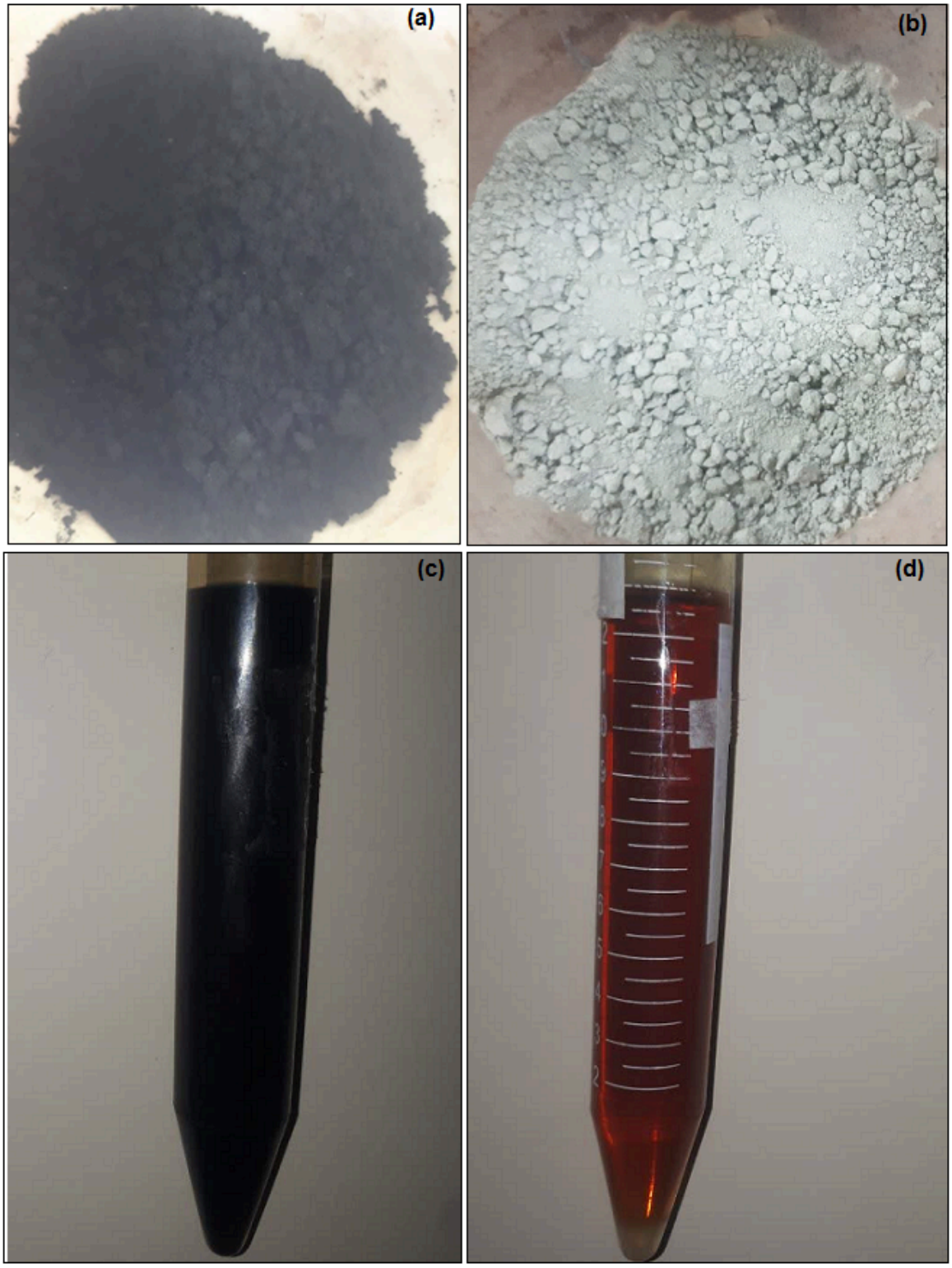


Figure 4

(a) Oil-saturated spent clay (b) Regenerated clay (c) Liquefied waste (d) Recovered oil

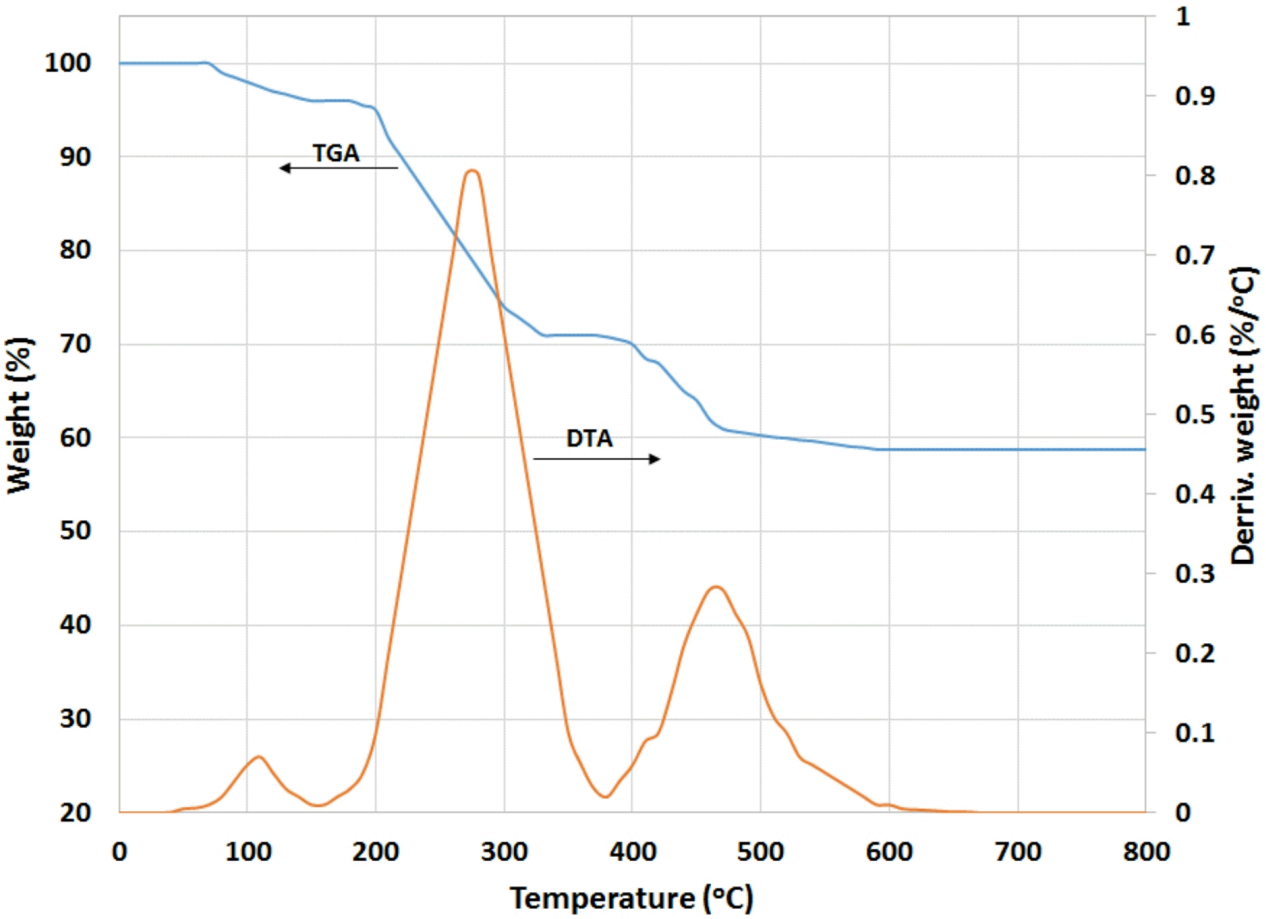


Figure 5

TGA and DTA diagrams of Oil-saturated spent clay

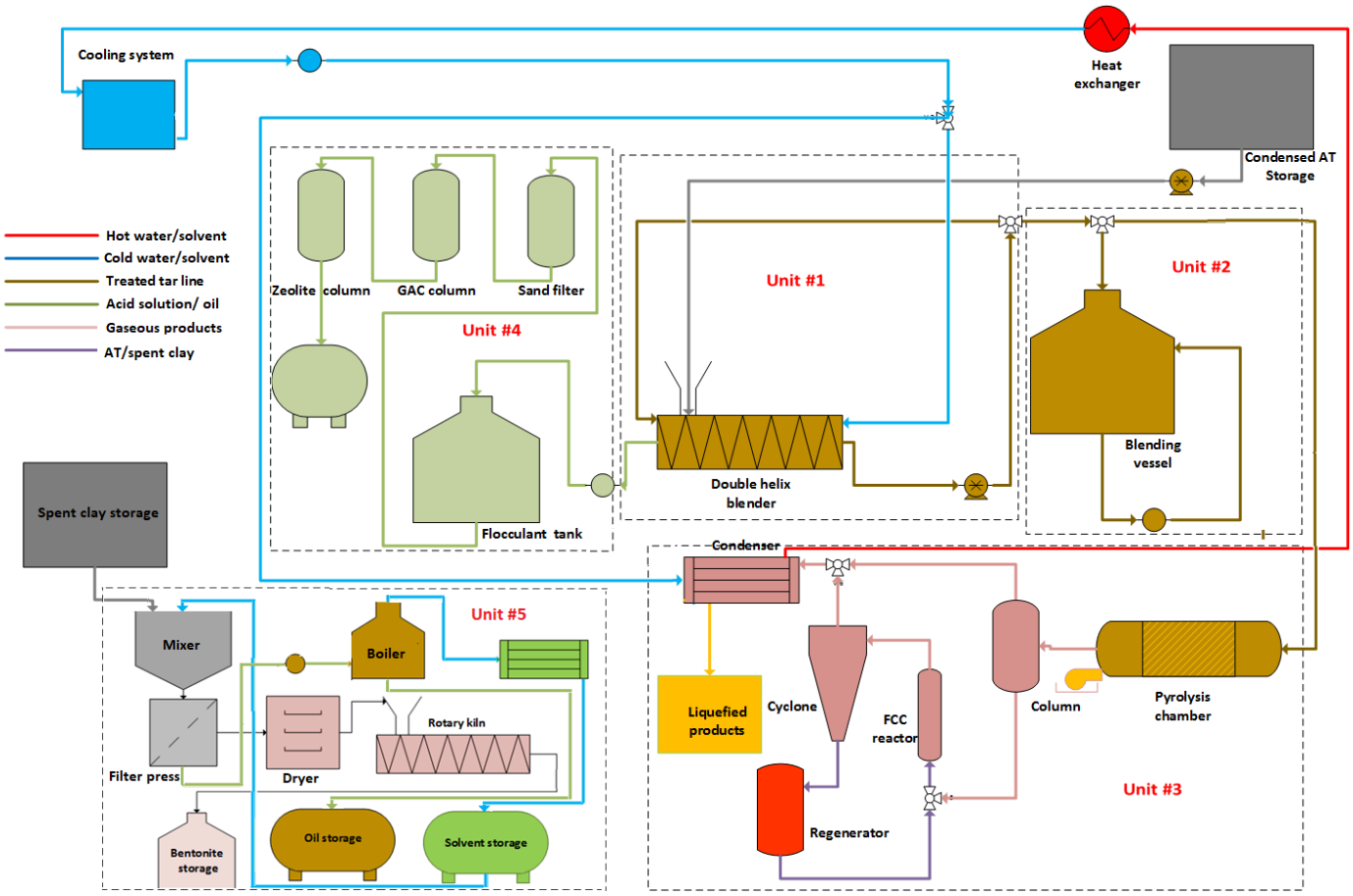


Figure 6

PFD diagram of AT treatment units; Unit #1: Acid/tar extractor; Unit #2: Rubber blender; Unit #3: Pyrolysis and catalytic cracking reactor; Unit #4: Acid water treatment system; Unit #5: Solvent recovery unit

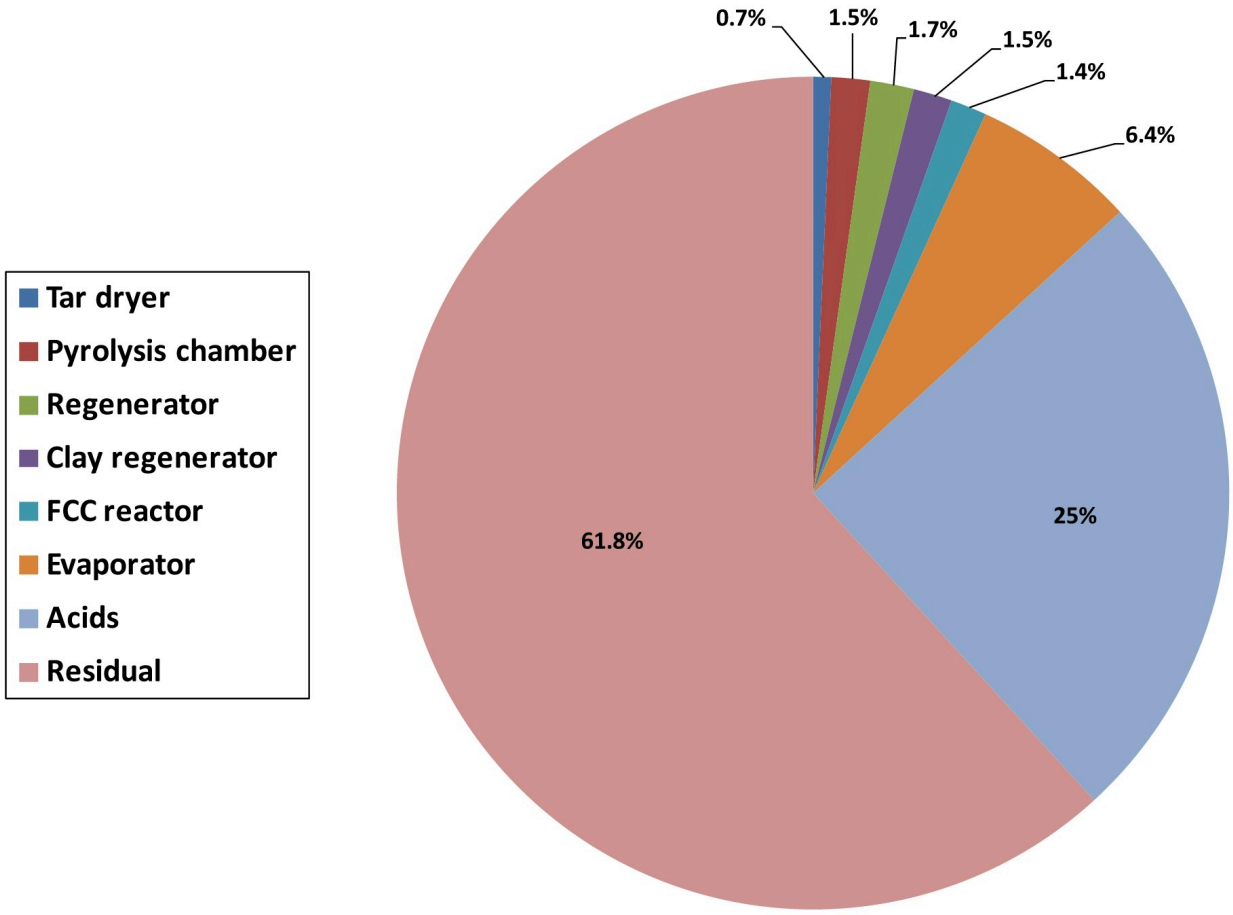


Figure 7

diagram of mass distribution of treated tar

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- table.docx