

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
27 December 2002 (27.12.2002)

PCT

(10) International Publication Number
WO 02/102930 A2

- (51) International Patent Classification⁷: **C10G**
- (21) International Application Number: PCT/US02/14089
- (22) International Filing Date: 2 May 2002 (02.05.2002)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
09/847,688 2 May 2001 (02.05.2001) US
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- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:**
— *without international search report and to be republished upon receipt of that report*
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*



WO 02/102930 A2

(54) Title: ENERGY EFFICIENT PROCESSES FOR CONVERTING REFINERY AND PETROLEUM-BASED WASTE TO STANDARD FUELS

(57) Abstract: The present invention is an energy efficient method for processing petroleum-based and other organic waste including sludge or bottoms, by utilizing of heat energy of oil shale ash or of other suitable ashes obtained from burning the solid fuel. The process produces no wasteful by-products like polluted sewage, heavy asphaltenics and tar by-products. Instead, the process eliminates water through selective adsorption by the ashes used as dewatering additives and the process is followed by drying at high temperatures. After skimming the dewatered matter, the remainder is processed by thermo-catalytic cracking by using hot oil shale ash or other ashes as a catalytic active material and as a heat carrier. The process uses equipment that is cost-effective and that is routinely produced. The process and apparatus of the present invention provide a solution for processing refinery and petroleum-based wastes and producing useful and standard liquid fuels.

**ENERGY EFFICIENT PROCESSES FOR CONVERTING
REFINERY AND PETROLEUM-BASED WASTE
TO STANDARD FUELS**

CROSS-REFERENCE TO RELATED APPLICATIONS

This Application is a Continuation-in-Part of co-pending U.S. Patent Application Serial No. 09/772,236 filed on January 29, 2001, the entire disclosure of which is incorporated herein by reference.

FIELD OF INVENTION

The present invention relates to the process of making a useable product out of refinery and other petroleum based sludge, bottoms, among others, and to the waste heat energy utilization with minimum environmental impact. Specifically, the invention is particularly suited to process waste of the type, but not limited to, slow moving emulsions and suspensions, containing organic matter and water with dissolved substances, and containing suspended particles and waste of heat energy. The present invention also provides an apparatus for producing useful and standard fuels from refining and petroleum-based waste.

BACKGROUND OF THE INVENTION

Finding a method to utilize refinery and/or other petroleum-based wastes, which represent, low mobility stable water emulsions with suspended solids, is a considerable problem. Currently available processes are costly, time consuming or inefficient and result in high waste by-products. A number of technologies have been described in the prior art.

U.S. Patent 4,624,417 of Gangi, et al. discloses a method for converting sewage sludge into various energy sources such as steam or methane gas and non-energy by products such as cement board, gypsum fiberboard, and agricultural products.

U.S. Patent 4,750,274 of Erdman, et al. discloses a method for improving the sludge drying by addition of large scouring particles. The scouring particles remove the particulate residue from the surfaces of the heat exchanger, where the sludge is heated. The heat transfer is also intensified.

U.S. Patent 4,786,401 of Jacob, et al. discloses a process for liquid sludge disposal by blending with the feedstock being passed to a fluid catalyst cracking. The sludge is premixed with hydrocarbons, such as light oil, prior to mixing with the feed.

U.S. Patent 4,897,205 of Landry is directed to petroleum sludge treatment by the use of steam and a re-circulating solvent with the purpose to decrease their viscosity and as a next step to separate the solid and the liquid components by settlement.

U.S. Patent 4,927,530 of Ueda, et al. is directed to sludge treatment in the special tank by the use of anaerobic bacteria.

GB Patent 2218256 and U.S. Patent 4,906,409 of Leister discloses a method in which sludge is dried in a fluid bed of preheated glass frit suspended in nitrogen. The dried sludge and glass is conveyed pneumatically (by nitrogen) to the verification device.

U.S. Patent 4,990,237 of Heuer, et al. discloses a method for oil recovery from waste oil sludge (pump-able, low viscosity, high oil and/or water-content sludge) by centrifugation of this type sludge. After that the centrifuge solids with low oil and water content are heated to volatize the contained water and oil. The oil and water are

condensed and separated by settling. The separated oil is centrifuged again and refined; the solids can be disposed.

U.S. Patent 5,022,992 of Looker discloses an apparatus for sludge separating by flotation for the floatable sludge.

U.S. Patent 5,246,599 of Aicher discloses a method and arrangement for sewage sludge treatment in closed system, where the treatment steps are connected by continuous passages in a closed system. The sludge is dried, converted by 250-350⁰C and finally sintered at least by 1250⁰C. The vapors removed in the drying stage and in conversion stage are condensed.

U.S. Patent 5,259,945 of Johnson, et al. is directed to the bottom waste processing by means of the vapor rapid stripping and by treatment of the heavy part of waste in a pyrolytic reactor for producing vapors, gases and solid residue, which may be used as fuels.

U.S. Patent 5,269,906 of Reynolds, et al. in addition to U.S. Patent 4,990,237 of the same inventors calcium oxide is used for the active sludge neutralization and nickel settling by the sludge processing.

U.S. Patent 5,271,851 of Nelson, et al. discloses a treatment system for refining oily sludge. The sludge is mixed with a particulate filter aid and with solvent selected from refinery products. The mixture contacts with a plate filter. A mixture of oil, water and solvent is produced as a filtrate. The filtrate is separated into an oil and water fraction. The oil fraction is directed to refinery. The produced water is routed to a refinery water treatment system. The filter coke residue is washed with a solvent, stripped to remove hydrocarbons and is removed for disposal.

U.S. Patent 5,324,417 of Harandi discloses a method for refinery sludge and slop oils upgrading over hot equilibrium catalyst removed from FCC regenerator. The hot catalyst demetallized and/or demulsifies sludge and slop streams in an auxiliary reactor and converts the sludge and slop oil hydrocarbons to more light products.

U.S. Patent 5,389,234 of Bhargava, et al. discloses a method for waste sludge disposal in a delayed coking process. In this order the waste at first is diluted with light hydrocarbons produced by delayed coking (naphtha or gas oil) to minimize fouling and foaming. The mixture stream is heated; the water and the light hydrocarbons are evaporated. The more heavy residue stream is heated to a coking temperature and is introduced into a coking drum.

U.S. Patent 5,428,904 of Rutz discloses a method for drying sewage by a gas with temperature up to 50⁰C. The drying gas itself is reconditioned by reducing its moisture in a separate circuit and is returned to the start of the process. The gas-drying agent (a hygroscopic material) is regenerated by withdrawing moisture there from.

U.S. Patent 5,466,383 of Lee is disclosed to treating dried sludge, also containing heavy metals. This process comprises indirectly heating the sludge in the absence of oxygen, up to temperature 300-550⁰C for organic material volatilization and heating the residue up to 750-1000⁰C together with steam for the non-volatile organic material gasification. The heavy metals remain in the ash as metal-sulfide complexes, which aren't soluble in acidic water.

U.S. Patent 5,573,672 of Rappas, et al. discloses a process for separating extractable organic material intermixed with solids and water by dewatering the mixture with dehydration additives in common with organic solvent and following separation the

organic solvent containing extractable organic material from the solids and hydrated additive.

U.S. Patent 5,580,391 of Franco discloses a process for the thermo-chemical cleaning of storage tanks by combined action of an organic solvent and the generation of nitrogen gas and heat, whereby produced heating in city, agitation and flotation of the fluidized sludge and its transfer to tanks or desalting units. It is assumed the matter can be reintroduced after that in the usual refining flow.

U.S. Patent 5,670,024 of Baltzer, et al. discloses a method for thermal treating of waste and residual material having coats of organic material by employing a drum-reactor developed for this process, heating the waste by a hot gas steam up to 850⁰C, evaporating and carbonizing the organic material and completely combustion the material.

U.S. Patent 5,681,449 and Japan Patent of Yokoyama, et al. discloses a method for treating an organic material containing solid sludge with water by means of heating the material up to 150-240⁰C by pressure to obtain a fluidized sludge and processing the fluidized sludge up to 350⁰C by 30-200 atm to convert the organic material to oil and after discharging separating oil from rest.

U.S. Patent 5,827,432 of Huhtamaki et al. is directed to sludge dewatering by electrically ionizing or by ultrasound treating and adding coagulant to the sludge to effect coagulation.

RU Patent 2106313 of Fokin, et al. discloses a method of drying petroleum sludge under vacuum at heat carrier temperature 120-140⁰C. Drying is performed in three steps: stripping water and part of sludge hydrocarbons, continuously feeding organic solvent (toluene, gasoline fraction etc.) and stripping excess solvent.

U.S. Patent 5,882,506 of Ohsol, et al. discloses a process for recovering oil from refinery waste emulsion by adding a sufficient amount of a light hydrocarbon diluent to the emulsion to lower its viscosity and specific gravity. The diluted emulsions are subjected to flashing at emulsion-breaking conditions after the oil is recovered.

U.S. Patent 5,922,189 of Santos discloses a process to refine petroleum residues and sludges generated by the oil producers, refineries and re-refineries comprising heating the mixture at this temperature for a time 1-6 hours for asphalt generating. The volatile products after condensation are directed to produce fuel, waxy oil and can be further processed.

U.S. Patent 5,961,786 of Freel, et al. discloses an apparatus for a fast pyrolytic system. The feedstock, non-oxidative transport gas and inorganic particulate heated material are rapidly mixed, than transported upward through an entrained-bed tubular reactor. The system includes a cyclonic hot solids re-circulation system and the vapor quenching system.

U.S. Patent 6,153,017 of Ward, et al discloses a method for treatment of soil contaminated with oil residues by means of forming aqueous slurry with hydrophobic foamed adsorbent (polymer or copolymer of styrene or other foamed materials having a density less than water). After mixing the adsorbent with sorbed oil is separated by gravity separation from the aqueous admixture.

DE Patent 19716436 of Matschiner is directed for used cooling lubricants reprocessing comprising: treating the lubricants with peroxo-di-sulphuric acid or their salts at 50-90⁰C, concentrating the sulphate-containing aqueous phase liberated from

organics. The concentrate is used for electrochemical production of peroxy-di-sulphate and the water is recycled back to the process.

U.S. Patent 5,672,277 of Parker, et al. discloses a method extraction of water by means of water-sorbing material that covers an inner surface of bag and presents in the bag as filaments.

U.S. Patent 5,676,711 of Kuzara discloses a process of conversion used oil to a low-sulfur diesel fuel processing the used oil with coal as an oil-coal slurry by 850⁰F and ~ 100 atm in a time more than 1 hour.

U.S. Patent 5,755,955 of Benham, et al. uses a hydro-cracking process with preliminary addition to the feed coke as an inhibitor and iron compound.

U.S. Patent 5,938,935 of Shimion discloses method and apparatus for purifying and treating cooling agents and/or lubricants used in the metallurgical industry. The solid particles are removed from the liquid by sedimentation on the plates, which are placed in specific manner, and additionally by magnetic force.

Gandi A.J. U.S. Patent 4,624,417, Nov. 25, 1986; Erdman Jr.A., Johnson J.C., Levad J.A. U.S. Patent 4,750,274, Jun. 14, 1988; Jacob S.M., Karsner G.G., Tracy III W.J. U.S. Patent 4,786,401, Nov. 22,1988; Londry K.C. U.S. Patent 4,897,205, Jan. 30, 1990; Ueda J. U.S. Patent 4,927,530, May 22, 1990; Leister P. GB Patent 2218256, June 03, 1990; Heuer S.R., Reynolds V.R. U.S. Patent 4,990,237, Feb. 5, 1991; Looker J. U.S. Patent 5,022,992, June 11, 1991; Aicher M. U.S. Patent 5,246,599, Sept. 21, 1993; Johnson, Jr., Satchwell R.M., Glaser R.R., Brecher L.E. U.S. Patent 5,259,945, Nov. 9, 1993; Reynolds V.R., Heuer S.R. U.S. Patent 5,259,906, Dec. 14, 1993; Nelson S.R., Claude A.M. U.S. Patent 5,271,851, Dec. 21, 1993; Harandi M.N. U.S. Patent 5,324,417,

June 28, 1994; Bhargava A. K., Louie W. S. W., Stefani A. N. U.S. Patent 5,389,234, Feb. 14, 1993; Rutz A. U.S. Patent 5,428,904, July 4, 1995; Lee K. U.S. Patent 5,466,383, Nov. 14, 1995; Rappas A.S.; Paspek D.S. U.S. Patent 5,573,672, Mar. 21, 1995; Franco Z.d., Khalil C. N., Pereira J.O.d. U.S. Patent 5,580,391, Dec. 3, 1996; Baltzer F., Juptner H. U.S. Patent 5,670,024, Feb. 6, 1995; Yokoyama Shinya, Kuiyagava Michio, Ogi Tomoko, Kebayashi Hideo, Minowa Towoaki, et al. U.S. Patent 5,681,449, Jan. 11, 1996; Huhtamaki M., Lehtokari M., Paatero J. U.S. Patent 5,827,432, Oct. 27, 1998; Fokin N.A., Kartashov M.V., Chernyshova N.E., Izmailov V.D. RU Patent 2106318, Oct. 03, 1998; Ohsol E.O., Pinkerton J.W., Gillispie T.E. U.S. Patent 5,882,506, Mar. 16, 1999; Santos B. U.S. Patent 5,922,189, July 13, 1999; Freel B.A., Graham R.G. U.S. Patent 5,961,786, Oct. 5, 1999; Ward O.P., Singh A. U.S. Patent 6,153,017, Nov. 28, 2000.

Thus, there are vast quantities of waste being produced worldwide that have the potential to be reused in a beneficial manner. The petroleum-based wastes can be processed to be used as gas and gas oil. There is a large niche in the market for the reuse of the intrinsically valuable waste stream. Efforts to develop a commercially viable resource recovery market have been hampered by problems of purification and high levels of impurities. The key to establishing this market is to process the inputs of sludge and petroleum-based waste in a single process, not relying on transport of materials and making a uniform output that is not contaminating the environment in a secondary manner.

It is accordingly an object of the present invention to provide an efficient, inexpensive, process and apparatus for converting sludge waste into standard fuels.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a process for the conversion of petroleum-based waste containing water, organic matter and mineral particles to liquid fuels or their components conforming to standard specifications and to utilize the waste heat energy of the heat (boiler's) assemblies.

It is a further object of this invention to provide a process that includes a method for dewatering the materials without the formation of sewage, and for dewatered matter processing without asphaltenic, or tar based wastes. The waste heat (of the hot ashes) from boiler's assemblies is used as a heat source for driving the process. The apparatus and process of the present invention have been described in detail by the accompanying figures, detailed description and specific embodiments of the invention below.

The primary object of this invention is to provide a process and apparatus able to handle variable waste loads in an economically viable manner.

There are other objects of this invention to produce a useable fuel, mainly gas and gas oil, and to utilize the waste heat energy, which in currently available method is wasted.

It is another object of this invention to provide a process and apparatus to remove the water from some of the waste materials such as highly watered refinery sludge and still keep a low level of viscosity.

It is another object of this invention to provide a process and apparatus to remove the water without extracting the highly toxic compounds, thereby obviating the need to clean the contaminated water.

BRIEF DESCRIPTION OF THE DRAWINGS

The process of converting petroleum-based wastes into fuels includes the features of the invention depicted in the attached schematic drawings which form a portion of this disclosure, wherein figure 1 is a flow diagram detailing option of the process and figure 2 details the inner workings of the reactor for petroleum based waste processing.

Fig. 1 comprises of a dewatering mixer unit (1), a reactor (2), a sieve (3), a bunker-portioner (4), and a fractional column (5).

Fig 2. represents a diagram detailing the inner workings of the reactor for the petroleum-based waste, the reactor (21), comprising a petroleum-based waste charge pipe (22), set of hoppers for the hot ash (23), a plurality of mixing elements (24), a pipe for cracking gases and vapors evacuation (25), a filtering system for gas-vapor and solid particles separation (26),

DETAILED DESCRIPTION OF PREFERRED EMBODIMENT

The invention provides the process of making a useable product out of refinery and other petroleum-based sludge, bottoms among others and at the same time utilize the heat energy present in the waste, so that there is minimum environmental impact. The treatment relates to the processing of slow moving emulsions and suspensions, containing organic matter and water with dissolved substances and suspended particles.

The overall process for treating the petroleum-based wastes comprises of the following steps:

- a. removing the water by the use of solid grain dewatering materials derived from hot industrial waste (hot oil shale ash or other suitable solid fuel ash, coal ash etc.) in the dewatering mixer (1);
- b. removing the water from the petroleum-based waste by water selective adsorption into the dewatering additives. These dewatering additives are protected from contamination by oils by controlling the introduction of the additives in accordance with the moisture of the raw material and in accordance with the kinetics of the water adsorption by the used additives;
- c. evaporating the adsorbed water without needing water expulsion, thereby avoiding the use of complicated and expensive equipment for the operation;
- d. treating the vapors formed by dewatering, with high temperatures of the hot ash stream outgoing from a boiler's furnace;
- e. skimming the processing material by means of adding heat as well as hot ash;
- f. decomposing the non-hydrocarbon components contained in the bottoms or treating them with alkaline-earth oxides of the oil shale ash or of other suitable ashes additives;
- g. processing the remaining petroleum-based material in conditions conducive to thermo-catalytic cracking by interacting with the hot catalytically active ash material coming out from a furnace; and
- h. desulfurizing the petroleum-based matter produced in the previous step by using the reactor. The reactor is operated under the unique control conditions of the present invention.

The petroleum-based sludges generally contain, up to 70% water. For example, in the sample that has been taken from sludge reservoirs at one refinery, the water content ranged within 57-68%. The sludge also contained 15-25% oil and 15-20% mineral particles.

The sludge is a stable oil-water emulsion and the mineral particles are suspended in the emulsion. The components of the sludge exhibit insignificant levels of settling, and therefore pose problems, for the dewatering step.

Current methods used for the separation of sludge mixtures include centrifugation, and organic matter extraction by solvent or flotation. These methods are expensive and create byproducts that are environmentally harmful. The water must be treated to remove impurities. Therefore the water evaporation method of the present invention is preferable, because it generates only pure steam, and not sewage, to be discarded into the environment.

Evaporation of the water from such a stable system as a petroleum-based waste is not possible by ordinary heating because of the strong interactions between the water/oil emulsions and the water expulsion. For some more water-based used lubricants the evaporation method referred to herein as, "in moving thin layer" is acceptable, but for the sludge it is not suitable because of the high viscosity of the materials. Moreover, these alternative methods described in the art are both expensive and inefficient.

An additional problem regarding the use of dewatering materials is that once the dewatering materials and petroleum-based waste are mixed, both the water and oils are adsorbed. As a result the water adsorption capacity of the dewatering additives is decreased and after several cycles becomes negligible. To regain the adsorption capacity,

dehydrating materials (CaO, CaCl₂, Al₂O₃, silica gel, etc.) are added to watered material and mixed. However, these dehydrating materials rapidly lose the ability to adsorb, and at the same time, cannot be recycled. Hence, the overall energy consumption requirement for dehydrating materials is increased.

The present invention bypasses these problems by creating a situation of selective adsorption of the water from the oil emulsion, while simultaneously utilizing inexpensive dewatering agents, by using such solid dewatering grain materials as oil shale ash or other suitable ashes.

The present invention is able to achieve selective adsorption due to the adsorption kinetics of the water and oil components. The adsorption capacity and rate is higher for the water component than for the oil component. So if the dewatering additive is linked to a variable feed mechanism then the optimal rate of application can be calculated. The advantage of this is that all of the additives are not applied at once and the water is completely adsorbed while the oil layer persists untouched. The dewatering material is then introduced depending on the program developed and is changed by varying the screw-feeder rotation speed.

The present invention also provides the procedure to determine the adequacy of a given material as a dewatering additive by the petroleum-based waste processing. To be considered as a suitable additive the materials must be shown to have been created as a by-product of another process. These by-products include:

- ☞ oil shale ash; oil shale coke-ash residue after the oil shale thermal processing - half- coking or retorting, gasification, etc.;
- ☞ suitable ashes from other solid fuels.

These and other like materials adsorb not only water selectively, but also oils. However the selective adsorption of water can be achieved by the procedure of the present invention.

The adsorption capacity of the oil shale ash of water is 65-70% by weight.

When the dewatering grain material granularity ranges within 1.0-6.0 mm that allows for separation of the material from the dewatered raw matter, and its mineral particles. The size of the mineral particles in processed petroleum-based waste is generally smaller than 100 μm . Therefore, variants of the conditions of the dewatering stage can be used depending on the dewatering material granularity.

By using the oil shale ash as a dewatering material, the process requires no separation and is therefore preferred and is simpler.

The dewatering material is introduced into the sludge in a controlled manner, and the water is adsorbed under suitable conditions. The mixture then consists of coarse dewatering particles impregnated by water, and the dewatered raw material.

The mixture formed is heated by adding the needed amount of the hot ash, and is dried. The procedure of drying runs without the expulsion of matter by heating. This is because the adsorbed water evaporates in (1) from solid particles. In this case the water-oil phase is destroyed by adsorbing the water to the dewatering material prior to evaporation. This type of separation of the emulsion is the key to successful evaporation.

The steam formed during drying is directed into the boiler (6), where the oil shale or other solid fuel is burned and is treated there at a temperature of $\sim 750^{\circ}\text{C}$. The organic substances, which can be captured by steam are decomposed and burned at this temperature. The amount of captured organic substance by this operation does not equal

more than 0.5-1% of the total. This mechanism may be used to successfully remove the organic based wastewater in form of pure and disinfected steam. This therefore avoids the expulsion of the watered matter during the heating process.

After the dewatering stage the mixture is directed into the reactor for carrying out several operations as enumerated below. The raw material is skimmed up to the cut-off point of 350⁰C.

The heat for the skimming is provided by the addition of the required amount of the hot ash, which serves as a direct heat carrier. Therefore, no additional energy is required and the process of the invention becomes economical.

After skimming, the treated matter is transferred into its activation zone (25). The hot ash is added into the activation zone for mixing, at temperatures of 350-380⁰C. At this stage the acidic sulfur and oxygen compounds of the sludge become decomposed.

The activated matter is then transported into the cracking zone where it is treated by the ash as a catalytic active material at a temperature appropriate for catalytic cracking. The composition of oil shale ash (the silica-alumina up to 30% and calcium oxide) makes it possible to carry out the thermo-catalytic cracking. The preliminary adsorbing of the organic matter into the catalyst (ash) grains, and the subsequent activation of matter, increases the intensity of the temperature, thereby reducing the heat consumption of the process. The net result is energy conservation.

The vapors and gases formed move out from the reactor and enter into the vortex chamber where they are cleaned to remove the captured ash dust.

The cleaned vapors and gases are separated by means of the fractional column (5), the gases are cooled, and the vapors condensed and cooled.

The ash and the coke formed (that deposits in the catalyst grains) are removed from the reactor (2) by means of the same mixer elements performing the task of both mixing and discharging. The residual ash contains no more 1-1.5% of coke and is directed into the main hot ash flow from the furnace.

The dust mineral component of a refinery sludge coated with coke (after the reactor) has been found to be useful in the cement industry. Its coke gives an added heat in the cement kiln, and its particles size and composition (SiO_2 , Al_2O_3 , CaO , Fe_2O_3 , etc.) are acceptable for cement production. It is clear that the dust and coarse catalyst separation after cracking process are suitable for this alternative application, when the dust particles are coated with the coke. In other cases it is reasonable to burn out the coke in the dust to use the dusty minerals depending on their composition and properties as filling or covering materials, etc.

The gases formed during sludge processing basically contain hydrogen, hydrocarbons, hydrosulfide and a very small amount of carbon monoxide and dioxides. All of the gases are burned in the boiler furnace (6) in common with oil shale. The sulfur oxide formed by the burning of H_2S is caught by the calcium oxide and calcium carbonate contained within in the formed oil shale ash and the sulfur oxide emission is prevented. In other cases the materials containing calcium carbonate are added to aid in the trapping of the SO_2 . Their presence, positively affects the cracking process and the desulfurization of the formed fuels.

Figure 1 shows the flow diagram of the process referring to **Fig.1**, the watery petroleum-based waste (sludge, etc.) is mixed with the hot ash, which is introduced by the controlled regime into horizontal mixer-dryer 1 with paddle mixing elements. The

mixture temperature doesn't rise more than 70°C . After the water is adsorbed by the additive grains, the matter is heated up to $150\text{-}160^{\circ}\text{C}$ by the hot ash which is added into the mixer-dryer through the other appropriate feeding system. The mixture is dried and the formed vapors are directed into the boiler furnace. Here they are heated and burned. The same procedure can be carried out in the boiler furnace (6). Often, the furnaces are fluidized bed burners.

The dewatered sludge is directed into reactor **2 (Fig.1)**. The reactor is a horizontal mixer with paddle mixing and discharge elements **(Fig.2)**. In contrast to the reactor, described in the parent patent application U.S. Serial No. 09/772,236, in this case the reactor isn't jacket heated. Instead the reactor is provided with a system (22) that controls the introduction of hot catalyst (ash) and with a hot filtering system for the separation of the dust. The processed material is therefore heated in three reactor zones by introducing hot ash into each of the zones.

In the first zone, skimming the petroleum-based material is carried out, with a cut-off point of up to 350°C . This is controlled by means of adding the appropriate amount of hot ash. The vapors are evacuated through the fractional column **5 (Fig.1)** that separate two fractions: (a) up to 210°C containing gasoline and (b) up to 350°C containing gas oil.

In the second zone, some non-hydrocarbon components are decomposed. This is followed by the activation of all remaining reaction matter, for example, the catalyst impregnated by remainder of the processed material. Furthermore, the hot catalyst is also added as a direct heat carrier.

In the third zone of the reactor, the catalytic cracking of the remaining material is carried out and the vapors and gases formed are evacuated through the fractional column 5.

The coke covered ash catalyst and dusty mineral part of the processed sludge are discharged from the reactor 2 by the same mixer elements and are separated by means of sieve 3. The coarser part of catalyst grains are directed to the mixer-dryer 1. The overall coke content 0.6-1.3% is not reduced. Neither is its adsorption capacity to water. The remaining part of the ash material is introduced into the hot ash flow, which is formed by the burning of the oil shale.

The petroleum-based waste processing can be organized as a batch process. Its advantage lies in the ability of the process to carry on the basic operation on the principle of "all operation in one reactor". It means that the dewatering stage can be carried out in the reactor, and after production of enough of the dewatered matter, the thermal processing (skimming, reaction matter activation, catalytic cracking) is carried out next in the same reactor. Thus this batch process is convenient for the small plants that need to process anywhere between 2-3 tons of material per hour on the basis of raw materials formed.

Examples

The equipment used for the process development and testing includes:

- ☞ a bench-scale unit with a horizontal, batch, heat reactor-mixer having a volume of approximately 7.5 liters, equipped with paddle mixer-elements suitable for dewatering, skimming and cracking the raw materials;

☞ a pilot plant including a horizontal heat reactor-mixer, having a volume of approximately 45 liters, (the sludge processing capacity is ~ 20 kg/h), suitable for dewatering, skimming and catalytic cracking the raw materials.

Example 1.

Processing of the refinery sludge with the composition, (mass %):

water	48.5
organic matter	28.7
solids	22.8.

The oil shale ash was used as a dewatering additive and as a catalytically active material.

The oil shale ash composition, (mass %) is:

SiO ₂	16.0	MgO	1.1
Al ₂ O ₃	7.9	Na ₂ O	0.3
Fe ₂ O ₃	3.3	K ₂ O	0.6
CaO	64.8	SO ₃	1.7

Oil shale ash from the reactor has a water adsorption capacity of about 61.3%.

This oil shale ash consumption on the sludge was about 80%

The sludge dewatering was carried out in a batch regime feeding the sludge, which allows for reliable water selective adsorption during the controlled introduction of the dewatering grain matter as it described previously in pending U.S. Patent Application Serial No. 09/772,236, filed on January 29, 2001, which is incorporated herein in its entirety.

The sludge mass of 3 kg was put in the batch mixer, with operating volume of 45 liters. The oil shale ash-feeding regime is estimated on the basis of the water adsorption kinetics and by investigating the mixing regularity. The used oil shale ash granularity was < 2.5 mm. When oil-shale ash is introduced in the reactor the temperature reaches up to 350⁰ C. After mixing 2.4kg oil shale ash with the sludge, the water is adsorbed by the oil shale ash grains, and the temperature of the mixture reaches 75.7⁰C.

During the next stage an additional amount 7.2 kg of hot oil shale ash, having a temperature 700⁰C, was introduced gradually. This results in the evaporation of water, and the mixture heats up to 155⁰C.

The dewatering vapors are directed into the boiler's burner.

An additional amount of oil shale ash at 700⁰C is introduced once again in the reactor containing the dewatered matter, for further processing, skimming and cracking of the oily material. The average temperature of the catalytic cracking was 410⁰C. The total amount of added hot oil shale ash in this stage was 22.7 kg.

The product yield was, mass %:

water	48.5
oil	20.1
solid product (mineral particles coke covered including 4.2% of coke)	27.0
gas	4.4.

The produced oil properties

Properties	Produced oil
Density (15.56 ⁰ C)	0.9035
Viscosity (40 ⁰ C), cSt	5.721
Sulfur	0.4
HHV, kcal/kg	10686
Water content	0.2
Ash	-
Stability	2
Metals content, ppm:	
Vanadium (V)	0.00
Nickel (Ni)	0.00
Aluminium (Al)	0.00
Hydrargyrum (Hg)	0.00
Plumbum (Pb)	0.00

The produced total oil conforms to standard for fuel oil of type light mazout.

Example 2.

Processing of the refinery sludge with the composition, (mass %):

water	18.1
organic matter	40.7
solids	41.2

The heavy sludge usually deposits at the bottom when the total refinery sludge is stored for a long time in special reservoirs. It looks like a very viscose oily material with visible solid mineral inclusions. By heating in the absence of air the sludge forms a strong caked mass which contains coke and mineral parts. This poses difficulties for discharging the remainder and for running the process continuously. However, addition of suitable amounts of water sorbent grains, provides for sufficient mobility of the processing matter.

The sludge mass of 0.5 kg is put in a reactor-mixer with operating volume 7.5 liters. The oil shale ash-feeding regime used corresponds to the water adsorption kinetics. An amount of about 0.16 kg of hot oil shale ash heated up to 400⁰C is introduced to initiate the water adsorption. This results in temperature of 73.4⁰C at the end of the process.

An amount of 0.52 kg hot. oil shale ash with temperature 700⁰C, is added gradually to raise the temperature to evaporate the water at 155^o.

An additional amount of oil shale ash at 700⁰C was introduced into the reactor holding the dewatered matter. This results in processing, skimming and cracking of the oily material. The catalytic cracking average temperature was 450⁰C. The total amount of added hot oil shale ash in this stage is 2.58 kg.

The product yield was, mass %:

water	18.1
oil	19.1
gas	5.3
coke	16.3
minerals	41.2.

The produced oil properties are:

density (15.56 ⁰ C)	0.8445	metals, ppm:	
viscosity(40 ⁰ C),cSt	2.1296	phosphorus	0.00
sulfur	0.35	calcium	0.00
HHV, kcal/kg	10900	magnesium	0.00
		zinc	0.01
		V, Ni, Cr	0.00

Although the present invention is described in connection with particular preferred embodiments and examples, it is to be understood that many modifications and variations can be made in the process and apparatus without departing from the scope to which the inventions disclose herein are entitled. Accordingly it will be understood that these embodiments are illustrative and that the scope of the invention is not limited to them. The present invention is to be considered as including all apparatus, systems and methods encompassed by the appending claims.

What is claimed is:

1. A process for treating petroleum-based waste material comprising organic matter, water, soluted substances or solid particles, said process comprising the steps of:

heating a portion of the waste material in the boiler furnace, to generate hot waste material including hot oil shale ash, solid fuel ash or coal ash;

removing water from the remaining petroleum-based waste by selective adsorption, using dewatering additives,

evaporating the adsorbed water by treating with the hot ash from the boiler furnace, thereby producing processed material, skimming the processed material by adding hot ash,

decomposing the non-hydrogen components with alkaline-earth oxides of suitable ash additives, inducing cracking with hot catalytic ash material, and desulfurizing the material produced, and collecting the gas vapor and oil fuel after passing the materials produced through a fractional column.
2. The process according to claim 1, wherein the dewatering process comprises of the steps of:
 - a) adding sufficient amounts of dewatering grain material to the waste material,
 - b) mixing and removing the water without contaminating the dewatering material by the petroleum components, and
 - c) drying the mixture by use of heat supplied by adding boiler's hot ash and directing the formed steam into the boiler, where the oil shale or other solid fuel is burned.

3. The process according to claim 2 wherein the dewatering materials are more coarse than the waste particles and the process further comprising the steps of:
 - a) separating by a sieve, said waste particles from the dewatered petroleum-based matter, and
 - b) directing the dewatering material with adsorbed water into the main hot ash flow from the boiler.
4. The process according to claim 1, wherein the dewatered petroleum-based material is heated up to 350⁰C in a heat reactor-mixer by the addition of the hot oil shale ash or by the addition of other suitable hot catalytically active material.
5. The process according to claim 1, wherein the dewatered material is heated by the addition of the hot oil shale ash or of a hot catalyst, and, wherein the reaction matter activation and the decomposing of non-hydrocarbon components is accomplished by heating at 350-380⁰C.
6. The process according to claim 5, further comprising:

catalytic cracking of the remaining material by addition of the hot ash as a catalytically active material and as a heat carrier, removing, separating and condensing the solid material and cooling the vapor and gaseous products.
7. The process according to claim 5, further comprising:

directing the gases for use by the boiler assembly where the oil shale or other solid fuel is burned, and catching the sulfur oxide formed by burning of gases by the alkaline-earth components of the formed ash.

8. The process of claim 1 wherein the catalytically active material for the catalytic cracking includes grain oil shale ash or other suitable ash
9. The process of claim 1 wherein the dewatering of the petroleum-based waste is done in combination with suitable solid additives in the reactor mixer, by a batch or a continuous regime.
10. A source of gasoline produced by the process of claim 1.
11. A source of gas oil produced by the process of claim 1.
12. A source of liquid fuel produced by the process of claim 1.

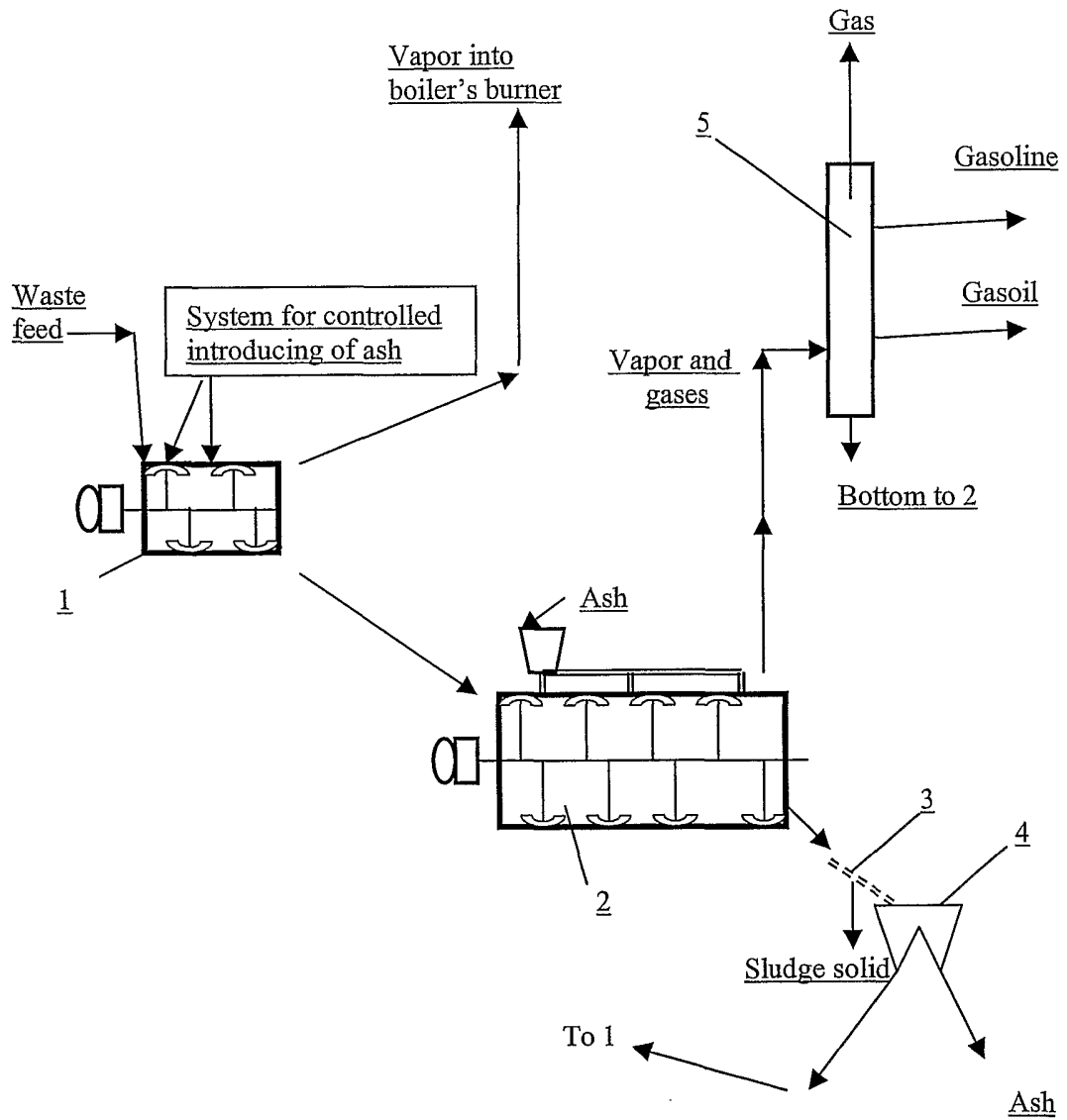


Fig.1. The process flow diagram.

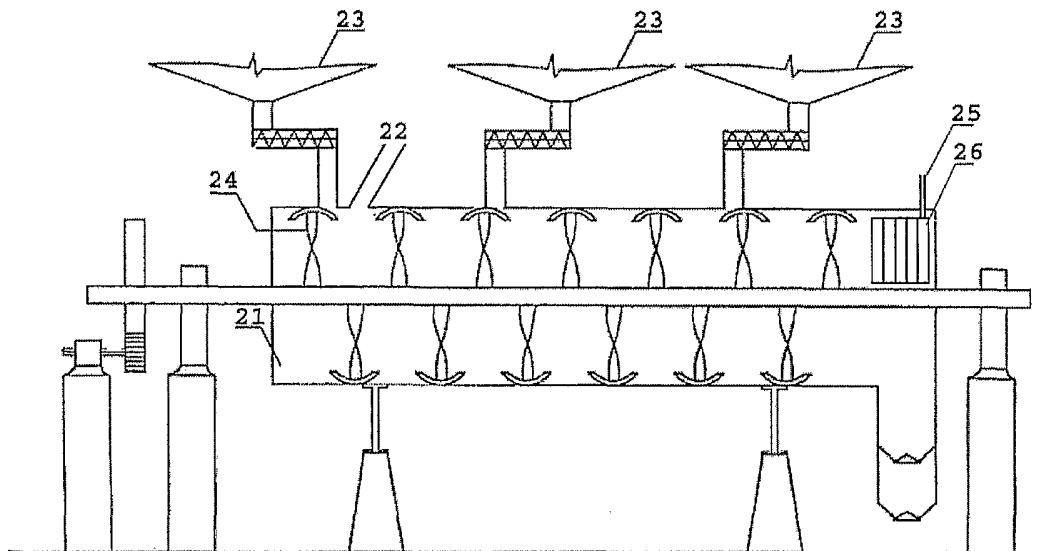


Fig. 2 Reactor for petroleum-based sludge processing