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Sludges and other organic by-products of industrial and community activity which present difficulties due to the presence of dispersed solids can be put to useful purpose with concurrent recovery, in whole or part, of inherent fuel values. Upon injection of such by-products diluted with added water to a delayed coker as aqueous quench medium, water content of the sludge is utilized to cool the hot coke. The dispersed solids and any organic liquids present are apparently dispersed through the coke mass, contrary to the expectation that these contaminants would be filtered out on the surface of the coke face first contacted thereby. The combustible solid portions of the by-product become a part of the primary fuel (coke). Non-combustible solids (e.g. sand, rust, silt) are distributed throughout the mass of coke in such manner that increase in ash content is acceptable as being within commercial specifications.

[21] Appl. No.: 495,460

[58] **Field of Search** 208/46, 127, 131, 370;

210/40

References Cited

2,773,003	12/1956	Brown et al.	208/370
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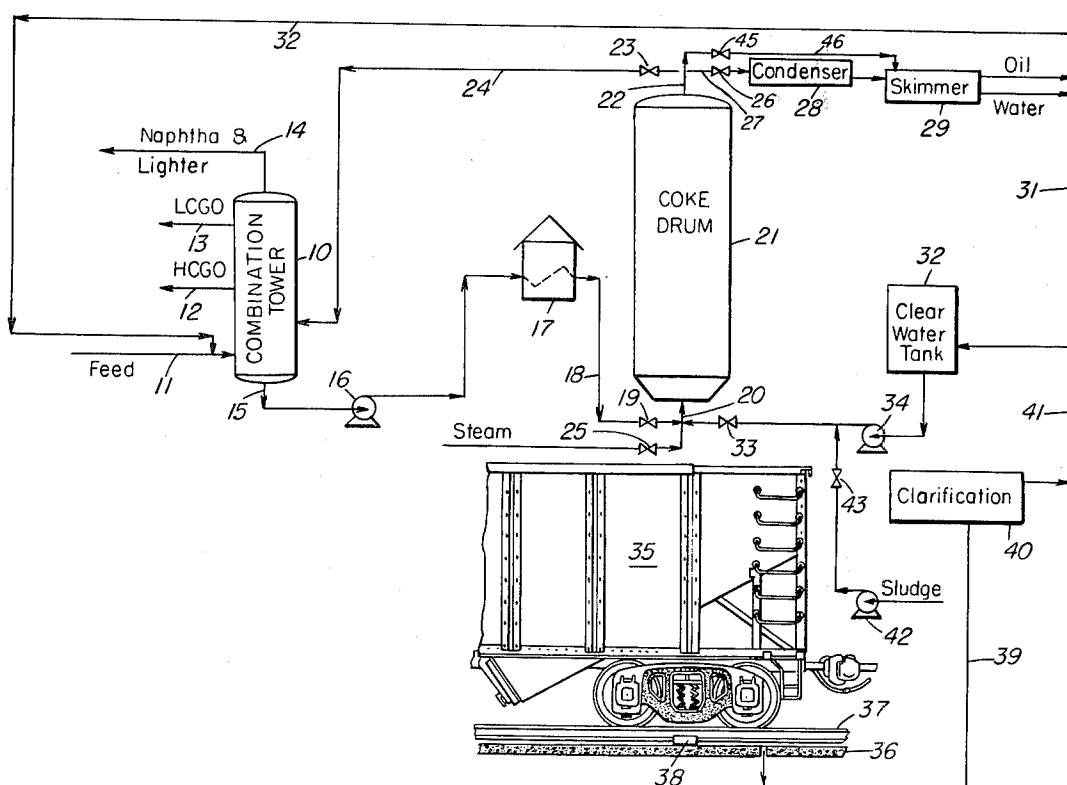
3,284,337	11/1966	Stoneburner	208/46
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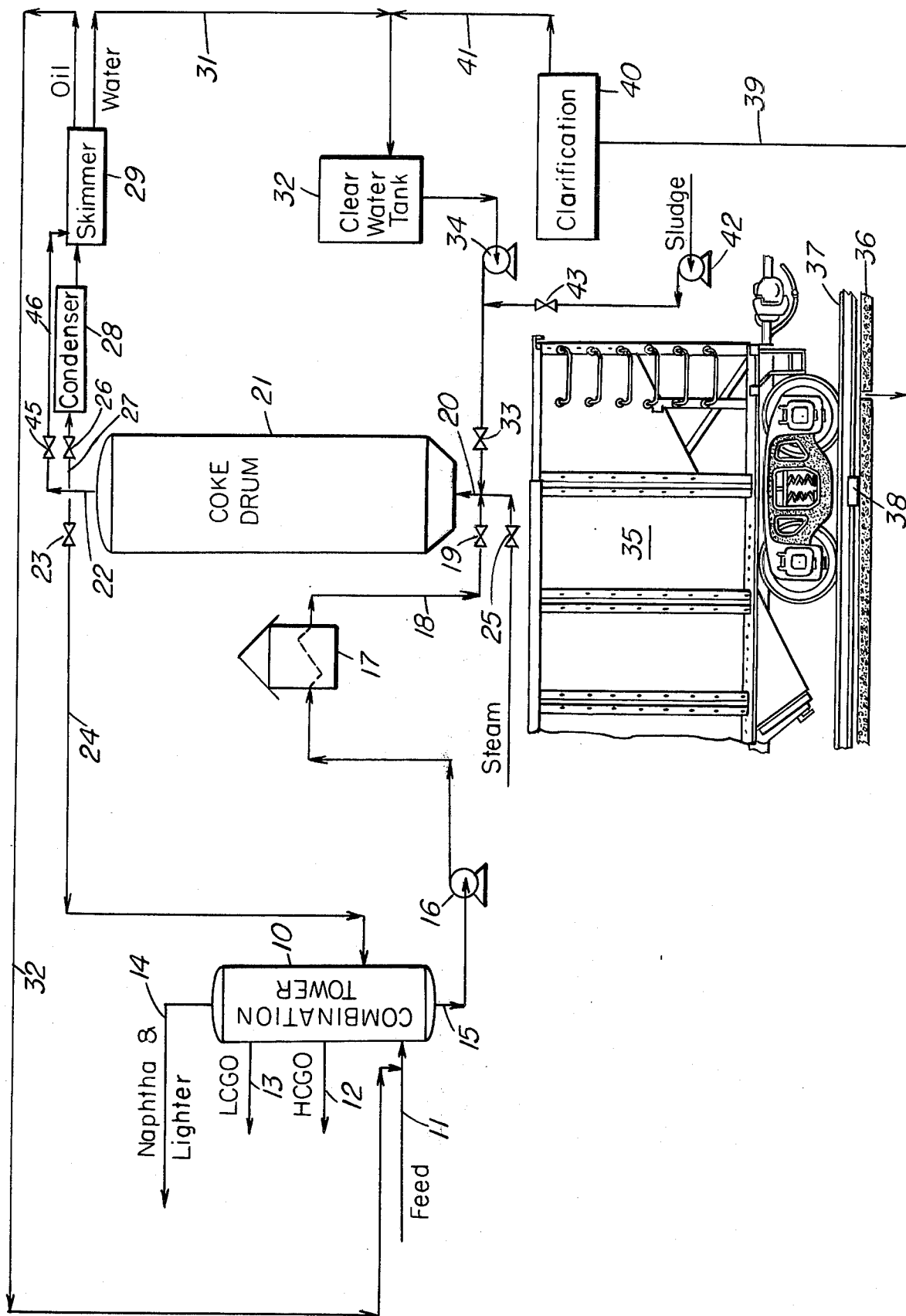
3,284,357	1/1968	Stonesamer	208/40
3,424,676	1/1969	Johnson et al.....	210/40

3,442,798	5/1969	Schoeffel et al.	210/40
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4 Claims, 1 Drawing Figure

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DISPOSAL OF INDUSTRIAL AND SANITARY WASTES

FIELD OF THE INVENTION

The invention is concerned with modification in two previously disparate industrial arts, namely (1) delayed coking of heavy petroleum fractions and (2) disposal of industrial and sanitary (biological) wastes.

SUMMARY OF THE PRIOR ART

Delayed Coking.

This refinery process is a means for handling very high boiling, viscous residues resulting from various petroleum refining unit processes. Such stocks are very difficult to process in other types of processes, due at least in part to the very low ratio of hydrogen to carbon which is characteristic of these stocks. Their use directly as fuel is restricted due to the fact that they cannot be pumped except at elevated temperatures or after dilution with lighter fractions of much greater value such as kerosines and light gas oils, thereby degrading the value of the "cutter stock".

The coker is therefore a means for converting low value by-products of petroleum refining into salable solid coke and light liquid products by a thermal cracking operation. Viewed another way, it aids in achieving stoichiometric balance in a refinery between the crude and desired liquid products. The latter have a higher hydrogen to carbon ratio than the crude petroleum input. By taking high carbon coke as one product, carbon is rejected from the remaining products, thus aiding in balance between input and products.

The delayed coking operation is cyclic in nature, operating a battery of coke drums which typically may be 18 feet in diameter and 83 feet high. The bottom of the drum is conical, closed at its bottom end by a flanged head which is removed once in each cycle. At the beginning of a cycle, the drum is heated, as by passing therethrough a portion of the hot vapors from another drum which is in the coking stage. As the drum reaches a suitable temperature, generally in excess of 500°F., charge stock from a heater is introduced through a pipe in the bottom head at about 900°F. At this temperature, the heavy stock undergoes thermal cracking to yield light hydrocarbons and coke. Any cracked product boiling below the temperature in the drum, say 880°F., will vaporize and is taken overhead through a vapor pipe in the top of the drum to recovery equipment for separation of products such as naphtha, kerosine, light and heavy gas oils as desired.

After about 24 hours, the drum is substantially full of porous coke in which the pores are filled with oil. Steam is then introduced through the bottom inlet to quench the coke. This achieves steam distillation of oil then present in the drum. During the early stage of steaming, the mixture of water and oil vapors continues to pass to product recovery as during the coking stage. Thereafter the effluent from steaming is diverted to blow-down facilities in which it is condensed and transferred to settling basins where oil is skimmed from the surface of the water.

After steam cooling to about 700°-750°F., water is introduced to the bottom of the coke drum to complete the quench. The first portions of water are, of course, vaporized by the hot coke. The resultant steam plus oil vapor is passed to blow-down for condensation and skimming to separate oil. Water addition is continued

until the drum is completely filled with liquid water. For a period thereafter, water is introduced to overflow the drum with effluent sent to settling equipment for removal of entrained oil etc.

The water settling system also receives water from other operations in the coker facility as later described. The clarified water so obtained provides the water for quench and for recovery of coke from the drum. Coke recovery proceeds by removal of top and bottom heads from the drum and cutting of the coke by hydraulic jets. First, a vertical hole is drilled through mass of coke to provide a channel for coke discharge through the bottom opening into a rail car spotted under the drum. Then a hydraulic jet is directed against the upper surface of the coke at a distance from the central discharge bore. The jet moves in a circle about the bore to cut the coke into pieces and then in larger concentric paths until a layer is cut away to the side wall. The cutting jet then repeats this operation at successive lower levels until the coke bed is completely removed.

The coke so cut from the drum appears in all sizes from large lumps to fine particles. To a considerable extent, the fines are separated from larger pieces as the coke discharges into hopper cars and water drains off through the hopper gates. This dispersion of fines in water is handled to recover the fines as solid fuel and the water returns to the system for use in quenching and cutting. It will be seen that the water cycle is a closed system in the sense that material added thereto may leave the coker installation only with the coke or with the liquid hydrocarbons produced by thermal cracking in the coke drums.

Sludge Disposal.

Modern manufacturing operations and modern methods for disposal of sanitary waste result in some materials which are extremely difficult to convert into innocuous or useful (recycled) substances at reasonable cost. A major problem of this nature is posed by mixtures which contain water and combustible, fine solids. Such mixtures are often called "sludge" and that term will be used herein for designation of materials treated by the technique of this invention.

Finely divided solids in liquids produce very stable dispersions and are also very effective stabilizers for liquid/liquid dispersions.

A typical sludge is that derived from activated sewage treatment plants which generally discharge an effluent of one weight percent solids. Dewatering techniques are known for concentrating the sludge but these are expensive and, at best, leave a concentrated sludge of high water content.

Petroleum refinery sludges are dispersions of oil and water having greatly different proportions of the two immiscible liquids stabilized by finely divided solids such as silt, sand, rust, high carbon content combustibles and the like. Such dispersions are not readily susceptible to emulsion breaking techniques.

These and other sludges have been subjected to various disposal techniques at considerable expense and less than uniform satisfaction. Incineration of waste containing substantial amounts of water requires elaborate and expensive equipment. The necessary washing of incinerator stack gases has the result that the end product is still a dispersion of solids in water, i.e. a sludge.

"Land Farming" is a technique for working sludges into land to permit final disposal by the slow process of bacterial action.

SUMMARY OF THE INVENTION

It has now been demonstrated that sludges can be introduced as part of the water quench to hot coke in a delayed coker. The first tests of this concept were conducted very carefully and under rigid control to permit immediate termination of the test in the event increased back pressure against the pumps or other extreme variations in operating parameters should indicate that solids released from dispersion or oil released from emulsification were accumulating at localized points to inhibit flow through the coke bed or produce extreme variation in coke quality. Such adverse result would not be surprising in a system in which the first portions are subjected to such temperature that water is immediately flashed off.

No untoward deviations were noted during tests. Sampling of the coke as removed showed only minor variations in ash and volatile matter in the coke during cutting at different levels in the bed. It should be noted here that the commercial scale coker in which the tests were conducted is not susceptible to accurate sampling without serious departures from normal operation. The results have been deemed adequate for future planning of commercial operation and the added expense of data capable of material balance has not been incurred. With caveat that the data here reported are not suitable for rigorous analysis of the operation, the data actually obtained are set out below as establishing validity of generalizations expressed.

DESCRIPTION OF PREFERRED EMBODIMENTS

The process of the invention is advantageously carried out in conventional delayed coker equipment, elements of which important to the invention are shown in the annexed drawing, consisting of a single FIGURE.

In the embodiment illustrated diagrammatically in the drawing, a single fractionation column 10 (the "combination tower") receives both fresh feed to the unit and vaporized overhead from the coking drum. Fresh feed, supplied by line 11 is any heavy petroleum fraction, such as residuum from crude fractionation, heavy recycle stock from catalytic cracking and the like. Generally, such stocks have boiling ranges above about 750°F. Desired products are separated in the combination tower 10. As indicated these may be heavy coker gas oil boiling above about 650°F., withdrawn at line 12; light coker gas oil boiling about 400°-650°F., at line 13; and unstabilized gasoline (naphtha and lighter gaseous products) at line 14.

A heavy bottoms fraction heavier than gas oil is transferred from the combination tower 10 by line 15 to pump 16, from which it passes through furnace 17 to be heated, for example to about 900°F. The heated charge is passed by line 18 and valve 19 to the inlet 20 to coke drum 21. The drum is one of a plurality, at least two, of such drums. By operating a battery of such drums in series, the system achieves continuous operation of the combination tower 10 and furnace 17; the hot charge being diverted to another drum in the battery when it is desired to discharge coke from a drum which has become full of coke on completion of the reaction stage of its cycle.

In drum 21, the hot oil undergoes an extended period of thermal cracking, often called "soaking". That cracking results in formation of volatile cracked products and coke. The material which is volatile at the temperature of the drum is withdrawn at discharge port

22. Valve 23 being open, the volatile products pass by line 24 to combination tower 10.

As the reaction stage is concluded, typically after about 24 hours, the drum 21 contains a body of porous coke having the pores filled by a heavy oil boiling above the temperature of the drum, usually about 880°F. Valve 19 is now closed and steam is admitted to inlet 20 by opening valve 25 in the steam supply line. Steam distillation occurs to remove most of the heavy oil in drum 21. In the typical embodiment being described, a first stage of steaming is conducted for 1.5 hours at 4000 pounds of steam per hour with valve 23 in open position, whereby the steam and oil vapors are transferred to the combination tower 10, together with cracked vapor from another drum then in the reaction stage. At the end of the first steaming stage, valve 23 is closed, and valve 26 in line 27 to the blow-down system is opened. The rate of steam is then increased to 15,000 pounds per hour and maintained at this level for 1.5 hours. As will be seen from the drawing, drum effluent during the second steaming stage passes through a condenser 28 and passes as liquid to settling basin and skimmer 29. The oil content of the drum effluent rises to the top of the water in skimmer 29 and is removed by usual skimming techniques to be recycled through line 32 to the feed line 11 of combination tower 10. Water from skimmer 29 is transferred by line 31 to clear water tank 32 for use as hereinafter described.

At the termination of the second steaming stage, the bed of coke is at a temperature of about 700°-750°F. Valve 25 is now closed and valve 33 is opened to permit entry to the coke drum of water drawn from clear water tank 32 by pump 34. Water so admitted is converted to steam in cooling the coke and the so generated steam passes by valve 26 to the blow-down system for return to the clear water tank. As the coke reaches the temperature of the water, water fills the voids in the bed of coke. The flow from the top of the drum may then be diverted directly to skimmer 29 by closing valve 26 and opening valve 45 to line 46 which bypasses the condenser 28. After liquid water has been flowed through the coke long enough to ensure adequate cooling, the drum is ready to be decoked.

Decoking proceeds by removal of flanged heads from top and bottom of the drum and cutting the coke by hydraulic jets. A railroad hopper car, indicated generally at 35, spotted below the drum, receives coke as it is discharged from the drum. The first stage of decoking is accomplished by drilling a bore through the center of the coke to provide a discharge channel. The hydraulic jet, not shown, is returned to the top of the drum after cutting the bore. It is then directed against the top of the coke while moving in a circular path concentric with and outside the bore. This cuts away lumps of coke which descend with water through the open bottom of the drum and into the hopper car 35. Water flows out of the bottom of the car 35 through the gaps at the hopper gates to be received in a sump lined with concrete 36 below the rail 37 and ties 38 on which the car 35 is supported. The water, which contains fine particles of coke, passes by line 39 to clarification equipment indicated generally at 40. Clear water from clarification is returned by line 41 to clear water tank 32.

In applying the invention to this conventional delayed coking operation, a sludge is added to the cooling water by a pump 42 through valve 43. The sludge preferably is supplied during that stage of water cooling when the coke is hot enough to vaporize the cooling

water.

It is found that sanitary sludges are handled to best advantage at the earlier stages of water cooling, while the coke is a high temperature, e.g., above about 500°F. Where sludges of both biological and oily types are to be handled, it is preferred that the biological waste from activated sewage treatment be injected with the first cooling water and oily sludge added later, total injection being completed before the coke becomes cool enough to begin filling of voids. Later injection will achieve some of the advantages of the invention but risks discharge of stubborn suspensions to the clear water tank. As will appear from data below, the stubborn suspensions are broken on hot coke with deposition of organic and solid components of the sludge on the coke, usually without exceeding specification limits for metallurgical coke, namely 15.0 wt.% volatile at 1800°F., 0.5 wt.% ash. As will be readily apparent, coke to be used as furnace fuel is subject to much more liberal specifications.

A series of five test runs were conducted under conditions of normal operation of the coke drum as described above. In each test run, contaminants were introduced with the cooling water under conditions such that temperature of the top of the coke bed was above 450°F., at the end of the test run. The test runs included operations in which a normally oily sludge from refinery operation and a normal biological sludge were used. The tests also included materials which are not normal sludges to evaluate effect of high concentrations of inorganic solids and hydrocarbons. The test runs are described in the examples below. In each case, water injection and decoking were normal.

EXAMPLE 1

The sludge in this example was a refinery slop emulsion containing 48 weight percent water. Hydrocarbon content consisted of 46.6 weight percent extractable by normal heptane (arbitrarily called "oil") and 1.2 weight percent soluble in toluene (asphalt). The residual solids after drying and extraction with normal heptane and toluene had the following analysis:

Volatile at 1800°F.	2.4 wt.%
Fe ₂ O ₃	0.4
FeSO ₄	0.5
SiO ₂	1.0

During introduction of 50 barrels of water from the clear water tank at start of the water quench stage, 50 barrels of the above slop emulsion were metered into the cooling water. Flow of cooling water was normal, without indication of unusual back pressures against the pumps. Samples were taken of coke during the cutting operation. While there is no way to be assured that coke delivered is entirely derived from the level at which cutting occurs, results in this and other test runs is good ground for confidence in the values reported, in that averages are all within specification values for metallurgical coke.

A sample taken during cutting of the top 1/3 of the drum showed a VCM (Volatile Combustible Material at 1800°F.) of 10.2 wt.%. Sample taken during cutting at the bottom 1/3 of the drum showed 8.9 wt.% VCM.

EXAMPLE 2

In this test, the same slop emulsion was injected as in Example 1; but at double the quantity, i.e., 100 barrels.

Inspection of coke during cutting showed average coke quality within specification:

VCM wt. %	Top 1/3	11.8
	Middle 1/3	10.8
	Bottom 1/3	18.5
	Bottom	11.8
	Average	13.2

EXAMPLE 3

This test introduced a hydrocarbon emulsion and fine solids suspended in water to attempt to trace distribution of these materials in the coke. Five thousand pounds of finely powdered barytes and 50 barrels of a 50% emulsion of paraffin wax in water were mixed with 50 barrels of water. The mixture was injected with quench water to the coking drum without abnormality of the quench operation. A very full analysis of coke sample was made to aid in understanding of the operation:

COKE	VCM wt. %	ASH wt. %	Ba wt. %
QUALITY			
Top 1/3	14.0	0.26	0.04
Middle 1/3	8.5	0.13	0.02
Bottom 1/3	9.9	0.21	0.015
Bottom	13.5	0.47	0.11
Average	11.5	0.27	0.05

EXAMPLE 4

Biological sludge (sanitary waste) from activated sludge treatment of refinery effluent water was dewatered to about 6 wt.% solids. Fifty barrels of the dewatered biological sludge were added to quench water to the coke drum. Injection was normal. The coke was within specifications for metallurgical coke:

VCM wt %	Top 1/3	11.3
	Middle 1/3	11.0
	Bottom 1/3	11.5
	Bottom Head	20.0
	Average	13.5

EXAMPLE 5

This test run was with a synthetic sludge containing a mixture of possibly troublesome materials to severely test the technique of this invention. The synthetic sludge was constituted by 50 barrels of wax emulsion (50% paraffin wax), 3000 pounds of powdered barytes, 7000 pounds of fine catalyst rejected from a Fluid Catalytic Cracker because of fineness, 100 barrels of water and 50 barrels of the dewatered biological sludge described in Example 4. Again, quenching and decoking proceeded normally. The coke showed abnormally high ash content with this abnormal synthesized sludge. Of particular interest is the distribution of ash:

COKE	VCM wt. %	ASH wt. %	Ba wt. %
QUALITY			
Top 1/3	7.7	0.42	0.027
Middle 1/3	17.9	0.77	0.046
Bottom 1/3	12.9	0.81	0.094
Bottom Head	11.5	0.33	0.020
Average	12.5	0.58	0.047

It will be seen that the invention provides a method for disposing of stubborn dispersions such as biological

sludge and oily sludge. These are characterized by finely dispersed solids and combustible matter. In the case of oily sludges, the dispersed solids are often non-combustible which become ash distributed through the coke product. The solids in some oil sludges may be themselves largely combustible. For example, in a refinery scheme which includes catalytic cracking of coker gas oils and coking of bottoms fraction from catalytic cracking can result in compounds of very low hydrogen/carbon ratio having a density greater than that of water. These can pass to the skimmer and there form a sludge with coke fines at the bottom of the skimmer. Such very troublesome sludges can be handled to good advantage by mixture with the coker quench water as described above.

The biological sludges have dispersed solids which are the combustible matter there present.

I claim:

1. A new use for a delayed coker in addition to its known operation wherein a body of hot liquid oil is maintained at thermal cracking temperature in an enlarged vessel for an extended period of time with discharge of cracked vapors for recovery of cracked product and accumulation of solid, porous coke in the vessel, whereupon the coke is steamed to reduce its tem-

perature and liquid water is introduced to the coke to quench it to temperature at which it may be recovered, initially at a coke temperature hot enough to vaporize the water and finally at a coke temperature such that water fills voids in the coke;

said new use comprising addition to said liquid water during the initial stage of coke temperature hot enough to vaporize the water of liquid sludge which contains dispersed combustible matter and finely dispersed solid particles which may be the said combustible matter; whereby the dispersion is broken with incorporation of combustible matter therefrom in the coke while conducting quenching and recovery of said coke.

2. A new use defined in claim 1 wherein said sludge is biological sludge from activated sludge treatment of waste water effluent.

3. A new use defined in claim 1 wherein said sludge is an oily emulsion with water stabilized by finely dispersed solids.

4. A new use according to claim 1 wherein water introduced to said coke is collected after contact with said coke to provide a source of liquid water to be introduced as aforesaid.

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