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Weber(10) **Pub. No.: US 2009/0120836 A1**(43) **Pub. Date: May 14, 2009**(54) **FCC-CFE CAT FINE EXTRACTION:
METHOD AND SYSTEM FOR EXTRACTING
CATALYST FINES FROM SLURRY OIL CAT
FINE BOTTOMS (SOCFBS) INTO AN
AQUEOUS LAYER****Related U.S. Application Data**

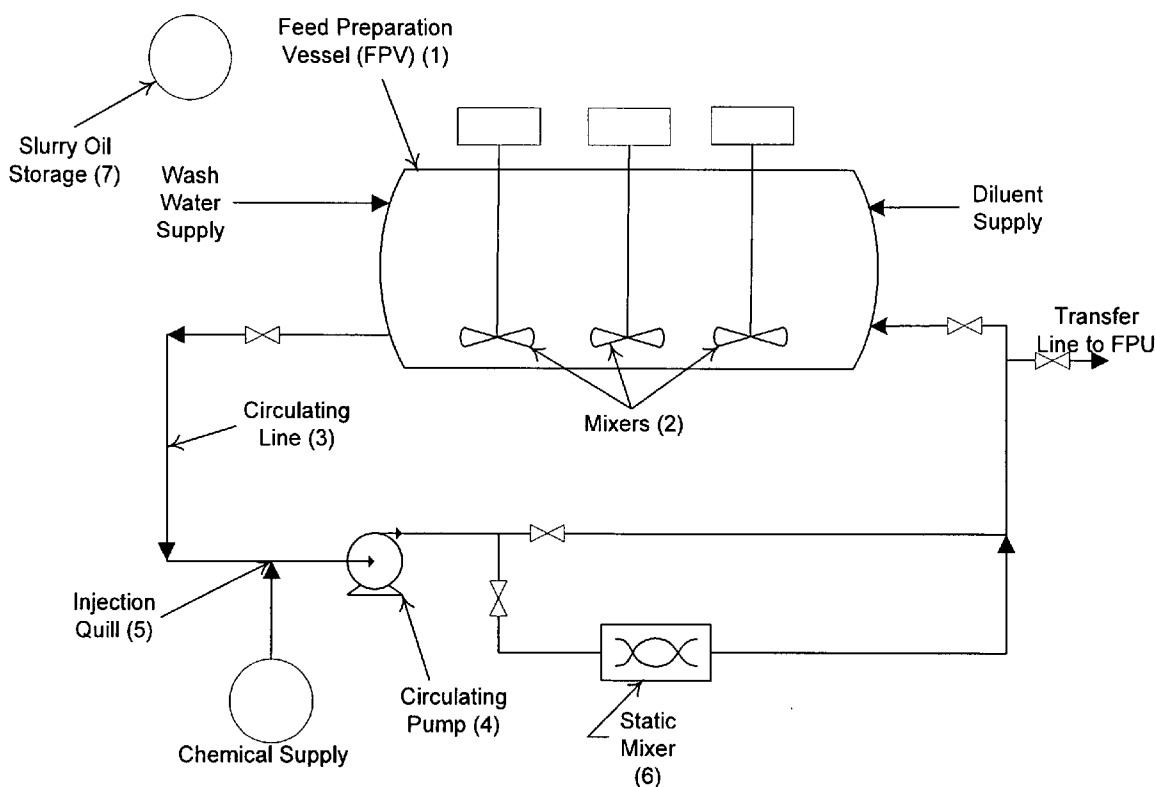
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C10G 21/02 (2006.01)(52) **U.S. Cl.** **208/13; 210/179**(57) **ABSTRACT**

A method for separating hydrocarbons from Slurry Oil Cat' Fine Bottoms (SOCFBs) comprising the steps of removing SOCFBs from a slurry oil storage tank and combining the SOCFBs with diluent and water in a Feed Preparation Vessel (FPV) and transferring the SOCFB and water emulsion to a Feed Processing Unit (FPU) in which the SCDM settles into a hydrocarbon layer, an emulsion layer and a water layer containing catalyst particles.

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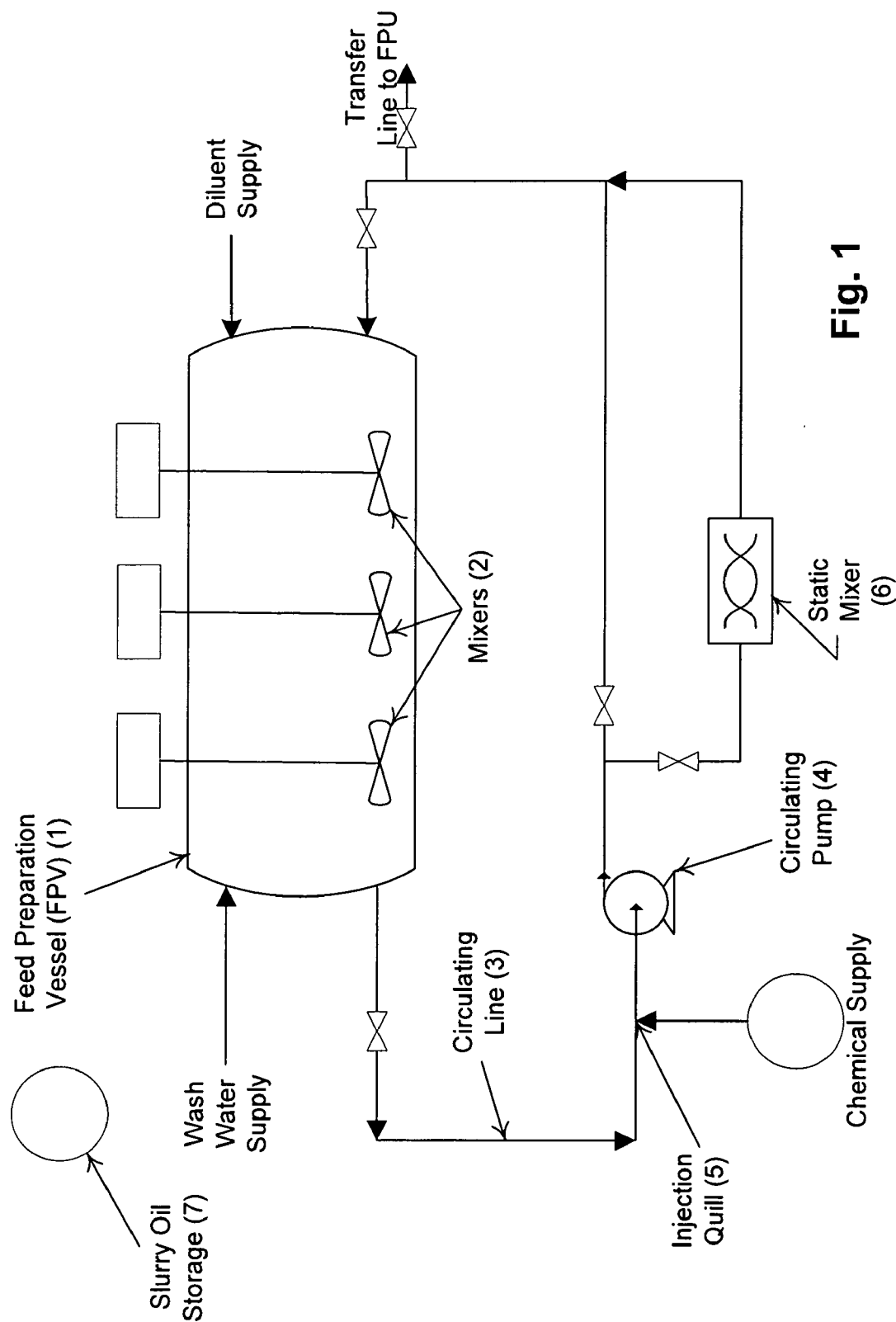
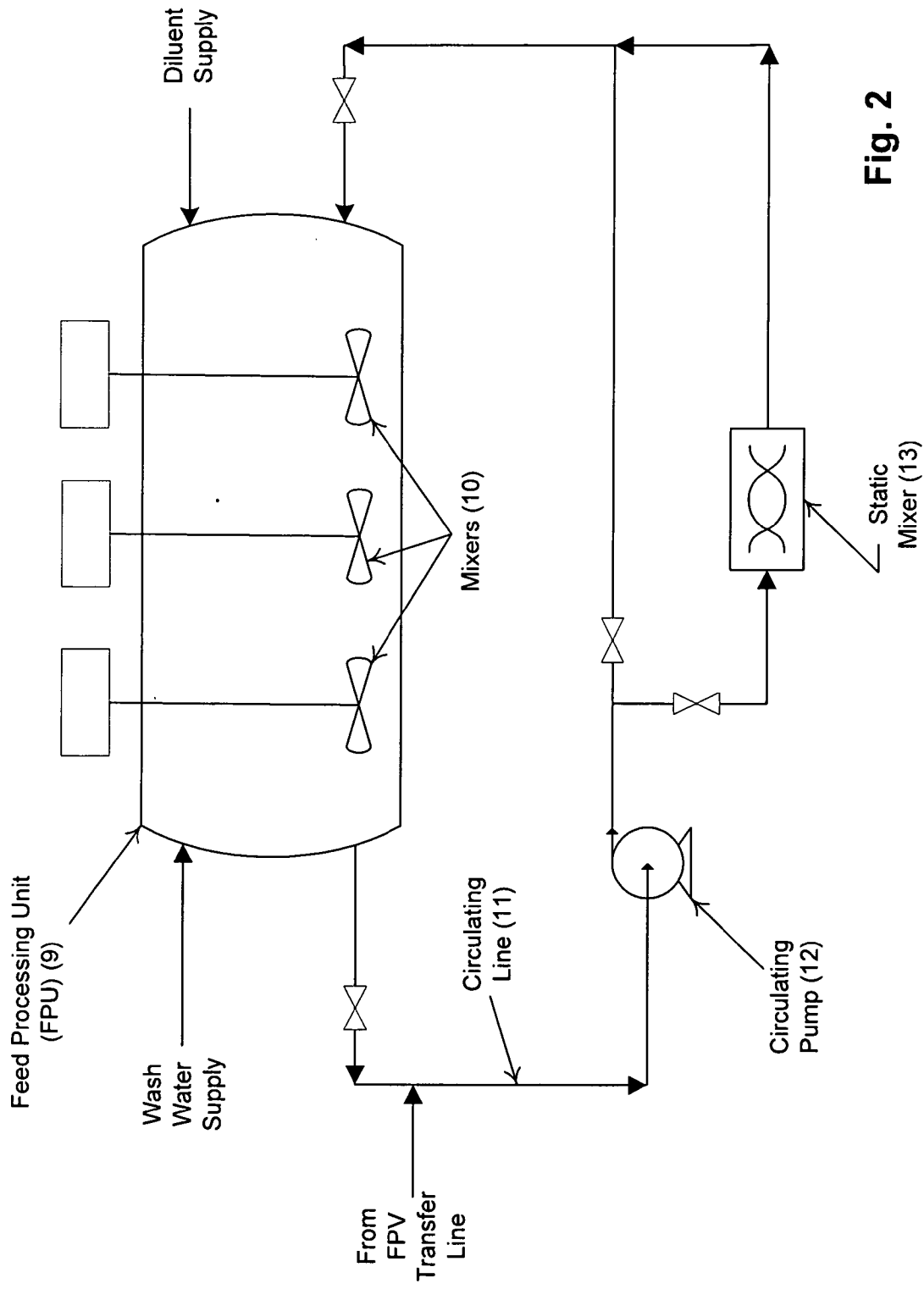


Fig. 1



**FCC-CFE CAT FINE EXTRACTION:
METHOD AND SYSTEM FOR EXTRACTING
CATALYST FINES FROM SLURRY OIL CAT
FINE BOTTOMS (SOCFBs) INTO AN
AQUEOUS LAYER**

FIELD OF THE INVENTION

[0001] The present invention relates to a system and method for the resolution of Slurry Oil Cat' Fine Bottoms (SOCFBs) into organic and inorganic components by the extraction of the catalyst fines from a prepared Slurry Oil/Catalyst Fines/Diluent Mixture (SCDM) into an aqueous layer. The invention is not restricted to SOCFB feed. The feed may be a diluted SOCFB feed, Cat Fine Cake resulting from centrifuge processing, a slurry oil run down stream, a SCDM or any hydrocarbon sludge.

BACKGROUND OF THE INVENTION

**Slurry Oil/Catalyst Fines Tank Bottoms Recovery &
Processing**

[0002] The problems presented by catalyst attrition from fluid catalytic cracking units (FCCU) have plagued the refining industry since the advent of fluid catalytic cracking in the first half of the 20th century. Over time, FCCU catalyst deteriorates in size. The size deteriorated catalyst is commonly referred to as catalyst fines.

[0003] In the FCCU process, cracked product stream vapor and some catalyst leave the reactor and enter the main fractionator near its base. On most units the bottom stream from the fractionator is called heavy cycle oil (HCO) or slurry oil. The term slurry oil has arisen as a result of the presence of catalyst particles in the tower bottom's product. For purposes of the present invention, it is sufficient to know that catalyst particles make their way to the slurry oil product storage tank. Slurry oil is a saleable product of FCCU processing. Once in the storage tank, the catalyst fines settle to the bottom, albeit very slowly. The layering of accumulated FCC catalyst fines that settles to the bottom of the slurry oil storage tank is referred to by the present inventor as Slurry Oil Cat' Fine Bottoms or SOCFB's

[0004] The existence of catalyst fines in the slurry tank presents a variety of problems to the refiner. The immediate and obvious problem has to do with product contamination. Slurry oil has proven to be an ideal feedstock for carbon black manufacture. Utilization as carbon black feedstock maximizes the value of slurry oil product. However, the presence of catalyst fines above a specified percentage in the slurry oil product results in an "ash content" in excess of that specification which is acceptable for use of the slurry oil as a carbon black feedstock. Even when the slurry oil product is utilized as a fuel source, a "price penalty" is effectively borne as ash content, in the form of the inorganic catalyst fines, increases.

[0005] Firms within the specialty chemical industry, which service the petroleum refining industry, have built proprietary product lines that serve to enhance settling of the catalyst fines. In recently or relatively recently cleaned storage tanks this procedure is typically successful in enabling the stored slurry oil product to meet even the rigorous specifications of carbon black manufacturers. As the accumulation of catalyst fines continues in the storage tank, a time comes when no amount of settling enhancement will permit the stored product to "meet specification" of carbon black manufacturers or even fuel products. A second dictate that compels the control

of SOCFB accumulation has to do with storage tank inspection criteria. Regulatory authorities require storage tank inspection at specified intervals. The presence of SOCFB's interferes with that exercise.

[0006] When accumulation of catalyst fines in the slurry oil storage tank becomes intolerable, in terms of meeting product specification or inspection criteria, refinery management schedules a clean-out. The clean-out is conducted under one of two typical scenarios. One type of clean-out, referred to as a "partial clean-out" calls for the removal of the catalyst fines without human entry. In this instance, enough of the catalyst fine sediment is removed to make the bottoms manageable once again. A second type of clean-out entails a complete removal of all catalyst fine sediment, subsequent human entry for complete clean up, a so-called mop-up, all followed by inspection, repairs and return-to-service.

[0007] The low API/high density of the slurry oil, coupled with the entrained catalyst fines, contributes to recovery and handling problems that are reputed to be some of the toughest in the tank cleaning industry. The tank cleaning industry has devised a number of procedures for catalyst fine removal from slurry oil storage tanks. These include the injection of diluent at high pressure either via side ports or from the roof, the cutting of "door sheets" using a water torch and various probe insertion devices. One such insertion device was co-invented by the present inventor and is called the SWEEPBER. It is the subject of U.S. Pat. No. 6,142,160, which serves the purpose of recovering catalyst fines from the bottom of slurry oil storage vessels. A diluent is required to enhance ease of handling of the catalyst fine bottoms in all instances known to this inventor. The observed diluent of choice is Light Cycle Oil or LCO, a side-cut of the FCCU fractionator.

[0008] The preponderance of catalyst fine projects, observed by the present inventor, are then conducted in a manner described as follows: As removal from the tank is carried out the typical procedure calls for transfer of the slurry oil/catalyst fines/diluent mixture (hereinafter SCDM) to a mobile mix tank, such as that supplied by Baker Tanks Inc., of approximately 22,000 gallons (approximately 500 barrels) capacity. The mix tank has the capability of heating the contents. A heated catalyst fine suspension of pre-specified temperature and concentration is then prepared, in the mix tank, as feed for centrifuge processing.

[0009] The heated feed is charged to the centrifuge and processed at a typical rate of 35 gallons per minute to 42 gallons per minute. Two streams result from the centrifuge process. One stream is referred to as recovered oil; the second stream is referred to as "filter cake" or "cat fine cake". The recovered oil is utilized per refinery management discretion. Typical options include blending the recovered oil into heavy fuel oil products or transfer to slop oil storage inventory for re-processing with the crude oil charge to the refinery crude unit via the desalter.

[0010] Pursuant to current U.S. Environmental Protection Agency guidelines, the filter cake is considered a hazardous waste. The cost of disposal of this cat fine cake has risen by ten fold since the mid 1990's and is expected to continue rising. The principal specification that governs the acceptability of filter cake pricing and disposal to a hazardous waste landfill is the "paint filter test". This test requires the absence of free flowing oil through a standard filter. However, despite the absence of free-flowing oil within the filter cake, a substantial

amount of hydrocarbon content remains within the filter cake and, thus, goes unutilized while it remains to impact the environment.

[0011] It is not unusual to find that the true hydrocarbon content of post-centrifuged filter cake is greater than 50%. It has been observed that filter cake of high melting point hydrocarbons, such as slurry oil, may contain as much as 83% hydrocarbon. The determination of true hydrocarbon content may be found by conducting a standard ASTM procedure for oil and grease or a true distillation.

[0012] There is a currently-used, second method of disposal for filter cake that renders the cake non-hazardous under EPA guidelines. The method is described in U.S. Pat. No. 5,443,717 issued to Robert M. Scalliet; et al. entitled "Recycle of Waste Streams".

[0013] A method for recovering the hydrocarbon component of SOCFB's has been invented by the present inventor and allowed as U.S. Pat. No. 7,244,364 and entitled "FCC-CFD Cat' Fine Desalting: A Method And System For Separating Hydrocarbons And Extracting Catalyst Fines From A Slurry Oil/Catalyst Fines/Diluent Mixture." FCC-CFD serves the purpose of recovering the hydrocarbon component of SOCFB's at a recovery rate of 99%+. However, "CFD" does not address the recovery and economic disposition of the catalyst component of SOCFB's. In the instance of FCC-CFD the catalyst component is extracted from the Slurry Oil Cat' Fines Diluent Mixture (SCDM) into the desalter water layer during the continuous refinery desalting process. This causes the extracted catalyst fines to mix with other solid contaminants, which have been extracted from the crude oil charge, and leave the desalter with effluent water which is directed to the waste water treatment plant (WWTP).

[0014] Alternatively, the present invention serves to both recover the hydrocarbon component of the SCDM while "hydrocarbon scrubbing" the catalyst or inorganic solids in the case of a more typical hydrocarbon sludge, and isolating the catalyst component, without contamination from other sources, into an aqueous layer. In the instance where the solids are FCC catalyst particles, these may be further processed in order to prepare the recovered catalyst for recycle through the refinery FCCU.

SUMMARY OF THE INVENTION

[0015] The present invention comprises a system and method of separating hydrocarbons from slurry oil catalyst fine bottoms. The method comprising the steps of removing SOCFBs from a slurry oil storage tank, combining the SOCFBs with a volume of diluent and water, and settling the diluted SOCFBs into a hydrocarbon layer, an emulsion layer and a water layer containing catalyst particles.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] FIG. 1 is a diagrammatic view of the Feed Preparation Vessel according to an embodiment of the present invention; and

[0017] FIG. 2 is a diagrammatic view of the Feed Processing Unit according to an alternative embodiment of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

[0018] While the invention is susceptible of embodiment in many different forms, there is described in detail preferred

embodiments of the invention. It is to be understood that the present disclosure is to be considered only as an example of the principles of the invention. This disclosure is not intended to limit the broad aspect of the invention to the illustrated embodiments. The scope of protection should only be limited by the claims.

[0019] The present invention comprises a method for separating catalyst particles from Slurry Oil Cat' Fine Bottoms comprising the steps of preparing a heated and treated Slurry Oil Cat' Fines Diluent Mixture (SCDM) in a specialized processing vessel referred to as a Feed Preparation Vessel (FPV) and transferring the prepared feed to a Feed Processing Unit (FPU). A SCDM is prepared in the FPV. Water is added to the SCDM and mixed in a manner predetermined by bench modeling the specific SCDM/water solution to ascertain a treatment formulation, a treatment dosage, mixing shear and ratio of the components, i.e. slurry oil cat fine bottoms, diluent and water. The water may optionally be treated with a water soluble demulsifier. After mixing within the FPV is complete and the proper temperature is achieved and while the mixture remains emulsified, the prepared feed is transferred to the FPU. Prescribed temperature is achieved in the FPU after which settling of the mixture in the FPU will yield an upper clean hydrocarbon layer, a minor emulsion layer at the water interface, and a lower water layer. The water layer will contain settled catalyst in the form of "scrubbed solids". "Scrubbed solids" refers to solid material, to include FCC catalyst particles, that have released adhering hydrocarbon from its surface and/or pores. The upper, clean hydrocarbon layer is then decanted leaving the minor emulsion layer and the water layer containing the scrubbed solids.

[0020] Upon achieving a satisfactory level of hydrocarbon scrubbing of the solids, be it catalyst material or inorganic solids; the scrubbed solids are transferred to a supplementary system of processing. The remaining water may or may not be used for subsequent processing or, alternatively, sent to a WWTP. The emulsion interface may or may not be charged to a subsequent processing batch or transferred to a storage vessel for further resolution.

[0021] In a broad overview of the present invention, the resolution of the components of Slurry Oil Cat' Fine Bottoms (SOCFBs), being the recovery of the hydrocarbon component of the SOCFBs and the extraction of the inorganic catalyst components of the SOCFBs into a water layer, are accomplished by mixing the SOCFB's with a predetermined amount of treated diluent and a predetermined amount of treated or untreated water, either/or both of which have been bench modeled to determine optimum treatment and dosage to enhance hydrocarbon scrubbing of the solids and enable a separation of the hydrocarbon and aqueous components into distinct layers.

[0022] In a typical exercise of the present invention two stages occur. These two stages are the feed preparation stage and the processing stage. The feed preparation stage prepares the heated and treated mixture. The processing stage includes extraction and separation of the components of the SOCFB or alternative feed. The requirement for two or even three steps of the process is dictated by the tenacity of hydrocarbon in clinging to and within the inorganic particles characteristic of the feed.

Bench Modeling

[0023] In order to utilize the present invention on a production scale, it is first necessary to optimize the processing

conditions through bench modeling of the specific SCDM/water mixture to be processed. After an appropriate bench model has been formulated, the bench model method is incorporated in the Feed Preparation Vessel and Feed Processing Unit equipment where further enhancements to the process may be performed.

[0024] Also, as a precautionary note, all laboratory testing should be conducted within the constraints of generally accepted laboratory safety procedures. Bench modeling requires the heating of water and semi-volatile hydrocarbon oil systems, which will result in increased pressure when heated. All containment vessels should be certified explosion proof for pressures anticipated by the procedure.

[0025] In order to perform the appropriate bench modeling of the intended processing parameters, samples of available diluent, water, SOCFBs or alternative hydrocarbon based feed to be processed, are procured. A choice is made as to the most desirable diluent blend in the context of diluent performance and availability. Demulsifier screening/optimization is performed by one skilled in the art of demulsification testing with the objective of determining demulsifier treatment that serves to best render a clean resolution of the oil and water layers with minimal establishment of an oil water interface. Demulsifier screening/optimization has the further objective of water-wetting the solid component, be it catalyst particles or other insoluble inorganic solids, while simultaneously causing a release of hydrocarbon from the surface or pores of the solid components of the feed. The diluent is treated with a demulsifier as determined by demulsifier screening/optimization. The sample of SOCFBs are added to the diluent and mixed. The resulting SCDM is then washed with samples of the wash water that will be used in the production-scale process.

[0026] As a starting point for the bench model it is preferred that an SCDM be prepared such that a 1 part addition of SOCFBs to 2 parts of the chosen diluent will result in a concentration of less than 20% Basic Sediment (BS) in the resulting SCDM. The present invention is not limited to 20% BS or to this ratio of dilution. Either may be varied in accordance with the Scientific Method. The SCDM is then heated in a water bath to a temperature comparable to that anticipated and authorized by refinery management. A typical temperature range will be from 160 to 210 degrees F. A volume of wash water, preferred as a starting point to be twice the volume of solids found in the SCDM, is added to the SCDM that has been heated to temperature. The entire mixture is then transferred to a standard laboratory blender and mixed. A preferred starting point for mixing is 30 seconds at mid level speed of the laboratory blender. After mixing, the emulsion is transferred to a calibrated vessel. The calibrated vessel containing the emulsion is placed in the bath and also heated to temperature. The quantitative and qualitative settling of the water layer and the extraction of solids into the water layer are observed and recorded. Based on these observations, appropriate changes in treatment, temperature, diluent concentration and mixing are made in accordance with the Scientific Method as dictated by the particular sample. Once the required level of hydrocarbon recovery and scrubbing of the inorganic solids are achieved, the parameters of the bench model are translated to the production scale.

[0027] Translating bench model results to commercial scale Practice.

[0028] Based upon the values determined in the bench model, commercial scale hydrocarbon recovery and inor-

ganic solids extraction of the mixed SOCFBs may be accomplished. As will be understood by one of ordinary skill in the art of demulsification, the conditions of the bench model should be repeated in the commercial scale process.

[0029] Referring to FIG. 1, there is shown a Feed Preparation Vessel (1) and a circulating line (3) in accordance with the present invention. The diluent is added to the FPV (1). The diluent is then circulated by mixers (2) and heated in the FPV to a temperature prescribed by the bench model. While circulating, the diluent is treated with a demulsifier blend from a demulsifier holding tank (8) determined by the bench model. Injection of the demulsifier takes place through an Injection Quill (5) in order to achieve the treatment dosage prescribed by the bench model. SOCFB's from a slurry oil storage tank (7), which may or may not have been diluted with diluent for purposes of retrieval from the slurry oil storage tank (7), are then transferred by pipeline or vacuum truck or other appropriate method and fed to the FPV (1) containing the pre-treated diluent volume in accordance with the bench model while mixing occurs with the FPV Mixers (2). The SCDM is mixed with the FPV Mixers (2) and heated to the temperature, dictated by the bench model. The SCDM may or may not be circulated through the circulating line with Circulating Pump (4) depending on the achievement of mixing as prescribed by the bench model. A volume of water is added as dictated by the bench model. The entire mixture is then circulated, while the Mixers (2) are operated, until such a time as an emulsion, consistent with that established in the bench model, is achieved. Increased emulsification may be achieved by routing the circulating SCDM/Water Mixture through a Static Mixer (6). Upon determination that the appropriate emulsion has been achieved; the SCDM/Water emulsion is transferred to the Feed Processing Unit (9) (FPU), shown in FIG. 2. Upon achieving a level of SCDM/water mixture above Mixers (10) within the FPU, the FPU Mixers (10) are turned on and transfer of the SCDM/Water emulsion continues to take place until the FPU (9) is filled and ready for processing of the three phases of the SCDM/Water emulsion. During transfer and filling of the FPU (9), temperature is maintained in accordance with the bench model

[0030] Upon filling to the desired volume and with prescribed temperature assured, the FPU Mixers (10) are turned off and the SCDM/Water emulsion is allowed to settle at the temperature dictated by the bench model. Settling in the FPU will yield an upper clean hydrocarbon layer, a minor emulsion layer at the water interface, and a lower water layer. The water layer will contain settled catalyst in the form of "scrubbed" solids. The upper, clean hydrocarbon layer is then decanted and transferred to inventory leaving the minor emulsion layer and the water layer containing the scrubbed solids.

[0031] A second processing step may optionally be performed after removal of the hydrocarbon layer. In the case of implementation of the secondary step, a portion of the water layer may be drawn off from the FPU (9) as prescribed by the bench model. A volume of additional water may optionally be added as determined by bench modeling. A volume of treated diluent, predetermined by bench modeling, is then added. The emulsion layer, existing water layer, scrubbed solids, treated diluent and any additional water are then heated and mixed in a manner predetermined by bench modeling. For a second time the resulting emulsion is left to settle and yield an upper clean hydrocarbon layer, a minor emulsion layer at the water interface, and a lower water layer. The water layer will again contain scrubbed solids. However, in this second step, scrub-

bing of the hydrocarbon will have been further improved, resulting in cleaner and more hydrocarbon-free solids. Upon the second settling, the upper clean hydrocarbon layer is again decanted leaving a minor emulsion layer and the water layer containing the scrubbed solids. Based upon the extraction of hydrocarbon scrubbed from the solids, as evidenced by the volume of hydrocarbon in the clean upper layer and by the extent of scrubbing of the hydrocarbon from the surface and pores of the catalyst particles; a repeat of this second processing step may be performed until the solids are scrubbed to a satisfactory degree.

[0032] Upon achieving a satisfactory level of hydrocarbon scrubbing of the solids (catalyst material in the case of SOCFB feed), the remaining clean hydrocarbon is transferred to its respective storage vessel. The scrubbed solids are removed from the FPU and transferred to a supplementary system of processing. The supplementary system of catalyst particle processing, may provide for drying and size classification of the catalyst particles as a preliminary to recycling through the FCCU. In an instance where hydrocarbon sludge, rather than SOCFB's, serves as feed to the FPU; the supplementary system of processing the inorganic solids, as opposed to catalyst particles, is envisioned to be drying and/or bioremediation. The economics of bioremediation are called into favor by the present method in that the hydrocarbon scrubbing of solids, characteristic of this invention, results in a lower volume of hydrocarbon to be remediated as compared to current methods of SOCFB or hydrocarbon sludge processing. After scrubbed solids are removed there remains some water and a minor emulsion layer. The water may be used in a subsequent processing step or sent to the WWTP. The minor emulsion layer may be utilized in a subsequent process or be removed and stored for further treatment and resolution.

[0033] While the specific embodiments have been described, numerous modifications come to mind without significantly departing from the spirit of the invention and the scope of protection should only be limited by the scope of the accompanying claims.

I claim:

1. A method for recovering hydrocarbons and extracting catalyst particles from Slurry Oil Cat' Fine Bottoms (SOCFBs) into an aqueous layer comprising the steps of:
removing SOCFBs from a slurry oil storage tank;
combining the SOCFBs with a volume of diluent to create a Slurry Oil/Cat' Fines/Diluent Mixture (SCDM);
combining the SCDM with a volume of wash water; and
settling the diluted SOCFBs into a hydrocarbon layer, an emulsion layer and a water layer containing catalyst particles.

2. The method of claim 1 further comprising the steps of:
removing the hydrocarbon layer; and
removing the water layer and catalyst particles.

2. The method of claim 1 further comprising the step of heating the SOCFBs and diluent to a predetermined temperature.

3. The method of claim 2 wherein the predetermined temperature is from between about 160 and 210 degrees Fahrenheit.

4. The method of claim 2 further comprising the step of combining the heated and diluted SOCFBs with a volume of water.

5. The method of claim 1 wherein the step of combining the SOCFBs with a volume of diluent comprises the step of adding and mixing the SOCFBs with treated diluent within a Feed Preparation Vessel (FPV) to create a Slurry Oil Cat Fines Diluent Mixture (SCDM).

6. The method of claim 5 wherein the step of settling the diluted SOCFBs into a hydrocarbon layer, an emulsion layer and a water layer containing catalyst particles comprises the steps of heating the SCDM to a desired temperature and combining SCDM with water.

7. The method of claim 6 wherein the mixed SCDM and water is transferred to a Feed Processing Unit (FPU) where settling occurs.

8. A system for separating hydrocarbons from catalyst fines in a slurry oil/catalyst fines/diluent mixture (SCDM) comprising:

a slurry oil storage tank;

a Feed Preparation Vessel (FPV) for receiving Slurry Oil Cat' Fine Bottoms (SOCFBs) from the slurry oil storage tank, the FPV further comprising a diluent feed inlet for introducing a diluent into the FPV and a mixer for mixing the diluent and SOCFBs into a SCDM; and

a Feed Processing Unit (FPU) for receiving the SCDM from the FPV and for settling the SCDM into a hydrocarbon layer, and emulsion layer and a water layer containing catalyst particles from the SCDM;

9. The system of claim 8 wherein the FPV is attached to a circulating line having a circulating pump attached to a static mixer for mixing the diluent and SOCFBs.

10. The system of claim 8 wherein the FPU further comprises mixers.

11. The system of claim 8 wherein the FPU further comprises a heater for heating the SCDM.

12. The system of claim 8 wherein the FPV further comprises a heater for heating the SCDM.

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