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(54) **Title:** RECYCLE OF ACID SLUDGE RESIDUAL IN HYDROCARBON REFINING PROCESS

(57) **Abstract:** This invention relates to the recycling of acid sludge which is byproduct of hydrocarbons treatment by sulfuric acid; this byproduct contains 5% to 85% sulfuric acid and 1% to 15% water and 5% to 20% of organic materials which are very miscible to each other. The invention provides an improved process for recycling of said acid sludge and converting it to fertilizer and bitumen's additive. In this process malodor and some dangerous compounds such as hydrogen sulfide and sulfur oxides are reduced or eliminated by bubbling air into sludge in temperature range 25 to 105 Celsius. Then by adding controlled amount of water and certain neutralizing agent to said sludge, two immiscible phases are formed which could separate quickly and completely. Lower phase contains soluble sulfate salt which is useful and vital for agriculture and upper phase contains organic sulfur compound which is applicable to the bitumen industry.

Description

Title of Invention: Recycle of Acid Sludge Residual in Hydrocarbon Refining Process

This invention relates to the recycling of acid sludge which is resulting from the treatment of hydrocarbons by sulfuric acid. most of the crude and major gas condensate, which are valuable product in the oil industry, have large amounts of sulfur compound in form of hydrogen sulfide and other organic forms, removal of these sulfur compounds, increases their value and leads to be valuable sulfur free hydrocarbon source. In general, many methods have been designed for removal of sulfur from petroleum hydrocarbons, each of which has some advantages and disadvantages. Equipment Simplicity, low investment, low operating cost, and eco-friendliness are the most important features which can overwhelm some processes, and obsolete the others. Among the various methods, the method of treatment with sulfuric acid in terms of equipment and operating cost, is the most desirable method, but in terms of the eco-friendliness, because of the byproduct of acid sludge, in some countries, it is limited and in others, it has been obsoleted for a long time. In this method, hydrocarbon is mixed with sulfuric acid, and most of the sulfur compounds are extracted and replaced from the hydrocarbon phase to the sulfuric acid phase. Empirical evidences show that, aforementioned method has the ability to reduce sulfur content, from 5000ppm to 200ppm during the refining of gas condensate. The ease of use and good ability of sulfuric acid to extract of polar molecules and various sulfur compounds, contributes to the widespread use of this method in same industries, including purification of waste lubricating oils. On the other hand, the presence of a dangerous acid sludge as a byproduct and the failure to achieve a suitable method for recycling or even disposing of said sludge, has cause the method to be obsolete and replaced it by some other alternative methods even with higher investment and more technical problems. For example, HDS or (Hydro Desulfurization) in very high initial investment and high operating costs and serious limitation of reducing of sulfur from very high concentration to very low, and inability to remove sulfur aromatic compounds such as thiophene and its other disadvantages, in many large industries, is still welcomed. At the same time, the ease of use and the very low cost of operating of the sulfuric acid treatment method, has led to widespread use it in many small industries, such as refining industry of waste lubricant oil. Unfortunately, failure to achieve a suitable method for the elimination or safe use of said sludge, is still a major challenge for these industries; So that some of them work informally and some in hidden from sight of environmental regulatory agencies.

The invented process is aimed at 100% elimination of the said sludge from the environmental cycle, providing the possible recycling unit with a simple equipment and low operating cost as well, which will be desirable and feasible for all industries involved by this sludge. In this process, the total amount of acid sludge, produced in a hydrocarbon purification unit, after simple operations, turns into two valuable

and beneficial materials, not only reduces the cost of hidden or abusive disposals, but also creates valuable material and make profits.

Technical Field

This invention relates generally to a process of converting acid sludge waste of hydrocarbon purification process by sulfuric acid to bitumen additive and fertilizer, more specifically, the invention provides low cost operation process to consuming acid sludge as a row material and producing two valuable materials; not only safe for the environment but also helpful in the agriculture and bitumen industries.

Background Art

During the last five decades, many attempts have been made, to transmute or recycle acid sludge; due to some limitations, in a comprehensive way, none of the invented methods have been able to solve the problem of this type of sludge. Here are some of the efforts and their limitations:

In 1936, William Herbert invented a process by heating acid sludge and converting it into three different types of products, including: sulfur dioxide, hydrocarbons and coke, the patented number is US2043646A. In this process, after heating at temperature of 500 to 1000 F, acid sludge is degraded and reaction products is separated by some equipment, which are introduced in the process. In 1960, Victor Brent claimed an inventive process, in which there are the same products (sulfur dioxide, hydrocarbon vapors, and coke), but in terms of the process, there are some differences, in comparison with US2043646A, which led to a new invention. The patent number was US2965558. Equipment complexity, high investment and high temperature operating are some disadvantages related to this type of invention.

Another work described in Patent number US3013860A is related to Herbert Jones who invented a process for production of crystalline ammonium sulfate from acid sludge which the claims exactly include the following steps: (1) admixing spent sulfuric acid sludge with recycled ammonium sulfate mother liquor whereby there is obtained an aqueous acid phase and an oil phase; (2) separating said acid phase from said oil phase; (3) contacting said acid phase with ammonia and simultaneously with an oxygen-containing gas, the amount of ammonia employed being sufficient to neutralize a substantial portion of the free acid in said acid phase and less than that required for reaction with all of the free acid in said acid phase; (4) admixing directly from step (3) the resulting acidic ammonium sulfate solution with recycled ammonium sulfate mother liquor while maintaining the resultant mixture at a pH below about 5; (5) partially dewatering directly from step (4) the resulting acidic mixture to obtain crystalline ammonium sulfate and ammonium sulfate mother liquor; (6) separating the ammonium sulfate crystals from the ammonium sulfate mother liquor; (7) recycling a portion of said mother liquor.The main disadvantage of this invention is large volume of circulating solutions which leads to large volume of some equipment such as storage tank, evaporator, crystallizer and centrifuge.

Patent number CA2116084C and US5573656A relate to Benjamin Santo, he invented A process for significantly decreasing the acid sludge settling time in waste oil recovery processes comprising the steps of heating used oil to a high temperature above 725 degrees Fahrenheit, cooling the heated oil, adding an oxidizing agent to the oil, allowing the acid sludge to settle within a period of approximately 24 to 72 hours, separating the acid-sludge-free oil from the acid sludge which settles out of solution as a result of addition of the oxidizing agent, and adding a polishing agent and separating the re-refined oil from the spent polishing agent. The spent polishing agent is recycled, and the acid sludge which settles out after oxidation is converted to either hard, oxidized asphalt or soft asphalt or asphalt products such as emulsions etc. some of disadvantages are: high temperature operating, long settling time and process constraint for acid-rich sludge which contain a large amount of acid, wasting lots of acid by consuming a large amount of neutralizing agent and a small amount of organic compounds for asphalt formation.

According to another invention in West Germany, No. DE1470452 (A1), the process involves the separation of acid sludge with water and a phenolic solvent; after mixing sludge with water and phenolic solvent, this mixture is allowed to separate into organic and inorganic layers. Organic layer is subjected to fractional distillation to separate phenolic solvent, which is then returned to be mixed with further acid sludge and water. The products of this process is dilute sulfuric acid and some valuable hydrocarbons. The disadvantages of this process include, the use of solvent and some problems related to multiple stages of recycling; the resulting sulfuric acid is diluted and cannot be reused generally as well.

According to the invention of CN102002411 , by adding lime to acid sludge and neutralizing it, granular solid fuel is formed, in this process during neutralization of the acid; a solid phase resulting from the formation of calcium sulfate is formed, which contains an amount of organic compound that can be used as solid fuel. The advantages of this invention are equipment simplicity and low temperature operation but the main disadvantage is producing a solid fuel which is useless for most of industries, another disadvantage relates to sludge with high sulfur content, resulting in serious air pollution because of burning sulfur. Finally the process is not useful for such sludge with low organic content.

In another patent No. US5049256A, in 1990, Mark C. Luce integrated solvent neutralization with methyl ethyl ketone, solvent evaporation, separation and reuse of methyl ethyl ketone, so he was able to provide a method for recovering hydrocarbons from acid sludge. Some problems and disadvantages of this process are similar to patent No. DE1470452 (A1).

In general, Equipment complexity, high operating costs, diversity of impurities in each acid sludge and problems related to transportation and maintenance of these types of waste, have led to reluctance of investment for creating a recovery unit.

Summary of Invention

An improved process for recycling of acid sludge and converting it to fertilizer and bitumen's additive. In this process malodor and some dangerous compounds such as hydrogen sulfide and sulfur oxides are reduced or eliminated by bubbling air into sludge in temperature range 25 to 105 Celsius. Then by adding controlled amount of water and certain neutralizing agent to said sludge, two immiscible phases are formed which could separate quickly and completely. Lower phase contains soluble sulfate salt which is useful and vital for agriculture and upper phase contains organic sulfur compound which is applicable to the bitumen industry.

Technical Problem

This invention relates to the recycling of acid sludge which is byproduct of hydrocarbons treatment by sulfuric acid; this byproduct contains 5% to 85% sulfuric acid and 1% to 15% water and 5% to 20% of organic materials which are very miscible to each other. Said organic part contains sulfur compounds such as hydrogen sulfide, sulfur oxides, thiophene, mercaptan, disulfide and etc. high content of organic sulfur compounds in said organic part, destroys the application of recycled hydrocarbons as fuel; and low price of sulfuric acid reduces the interest in recycling it, particularly at high operation cost and high total investment. So all the costs and efforts, just related to solving the environmental problems. In conclusion, high investment and high operation cost have led to a reluctance to invest and subsequently environmental pollution.

Solution to Problem

In this process, the total amount of acid sludge, after simple and low cost operations, turns into two valuable and beneficial materials. The first step includes exhausting hydrogen sulfide with bubbling air inside the reactor, during this, the odor decreases as well. In the next stage we use some cations which have two features, first, they must be able to make molten salt or saturated solution, and second, they should be useful for agriculture. We found that immiscibility of molten salt or saturated solution of said salt, with sulfur organic compound is very dependent upon temperature and composition of molten salt. Magnesium sulfate hepta hydrate is a suitable matrix for this system due to the absence of a clear boundary between the its molten salt phase and its aqueous saturated phase. Adding small quantities of zinc, manganese, iron and ammonium to molten salt cations leads to the displacement of eutectic point of molten salt. Therefore, the presence of several certain cations, both in terms of agriculture and in terms of physical and chemical status of matrix, is an effective point. After separation of two inorganic and organic phases by suitable separator, there are two beneficial materials. A multiple cations salt which is very useful in agriculture and some sulfur organic compound which is very useful for bitumen industry. The presence of organic sulfur compound in bitumen not only eliminates its environmental problem, but also can affect and modify the properties of it; due to the reactivity of the sulfur functional groups in said organic phase with the bitumen's compounds.

Advantageous Effects of Invention

In summary, the advantages of this invention over previous inventions are as follows:

The entire volume of acidic sludge is completely converted into two precious substances and there is no residue for this process. No organic solvents or any other costing material has been used therefor initial investment and operating costs are very low. The aforementioned advantages can lead to the further revival of the hydrocarbon purification process with sulfuric acid which is obsoleted or restricted because of said acid sludge.

Brief Description of Drawings

According to figure 1, first by bubbling air or adding oxidizing agent in weight range of 0.5% to 5% of acid sludge waste, hydrogen sulfide and some odorous compounds exhaust easily, afterwards the reaction is carrying out in presence of 50 to 80 parts of acid sludge as raw materials, with 10 to 50 parts of magnesium, ammonium, zinc, iron and other cations suitable for agriculture or other related industries, as a neutralizing agent, and 0 to 200 parts of water as a crystallization agents, in temperature range of 50 to 105 Celsius. In this situation two immiscible phases are formed and then separated rapidly and completely, due to a significant difference in density and incompatibility with each other; inorganic lower phase which is molten or saturated sulfate salt is sent to the fertilizer storage tank then to the dryer. Organic upper phase which is molten organic sulfur compound is sent to the bitumen's additive storage tank. Both phases could be solid at lower temperatures.

According to figure 2, acid sludge as a main feed is pumped through line 14 to receiver vessel 16 for a longer time maintenance. At the beginning of operation, acid sludge is transferred into the main reactor 21 through line 18. Then through line 39 certain amount of water is added and by blowing steam and air in lines 24 and 25, at 25 to 105 Celsius, some sulfur compounds, including hydrogen sulfide, sulfur oxides and other volatile odorous compounds can be oxidized or easily removed from the reactor 21 and materials become safer and more odorless. During this process agitation occurs by agitator 20. Through line 36, air and toxic, is transported to the absorption tower 35, toxic gases is emitted from the air by reaction with neutralizing or trapping agents such as sodium hydroxide or lime which circulates in the tower by a pump 36. Air enters to the atmosphere through line 38. Driving force is supplied by sucker fan 37. According to figure 2, after the aeration, water and neutralizing agent, enter to the reactor from mixer 13 simultaneously and the temperature is controlled in the range of 50 to 105 ° C. After completion of the reaction, two phases including molten or saturated inorganic phase with organic sulfur phase, form and dissociate rapidly. By line 22, the lower part which is molten or saturated inorganic phase, is transferred to the inorganic phase storage tank 26, by line 23, and the upper part which is organic phase, is transferred to the organic phase storage tank 27, by line 24. This liquid displacement is accomplished by the suction, provided by the vacuum pump 40 in the lines 41. The produced salt

(which can be used as chemical fertilizer or industrial salt) goes to the dryer 29 from storage tank 27 and becomes soluble crystal or dry powder. The organic phase is also packaged for bitumen additive use.

Examples

The amount of 200 kg of acid sludge derived from the hydrocarbon purification process, which is analyzed in the laboratory, contained about 70% sulfuric and 20% organic sulfur compound and 10% water; at the first step the air is introduced to the reactor by bubbling for 4 hours at a flow rate of 100 liters per minute; after reducing odor and toxic chemicals to acceptable levels, the second step is 130 kg of water for crystallization of magnesium sulfate and then 15 kg per hour of magnesium oxide is added continuously until two immiscible phases are formed; at this situation agitation continues for 15 minutes and then organic phase which is located in the upper part guides to bitumen's additive storage tank and inorganic phase which is located in the lower part, first guides to its storage tank and afterwards to the dryer.

The same example was performed, except that with using 85% magnesium oxide, 10% ammonium hydroxide and 5% zinc oxide on stoichiometric scale with available acid in sludge, were used.

Industrial Applicability

The main application of this invention is summarized in two sections:

The first is, large amounts of fuel hydrocarbons containing sulfur could not refine, because of technical and financial problems, this invention helps and makes reassurance to create more refining units of said fuel hydrocarbons by sulfuric acid method.

The second relates to some industries which use desulfurization process by sulfuric acid and still are involved in problems and costs of produced sludg.

Claims

[Claim 1] A process for recycling acidic sludge which is byproduct of petroleum hydrocarbons refining process, comprising: A) Degassing operation of sludge by suitable gas or oxidation operation of sludge by reacting with air or common oxidants, in the weight range of 0% to 5% of oxidant and in the temperature range at 25 to 105 Celsius. B) Mixing operation of 50 to 80 parts of said sludge with 10 to 50 part of such compounds which contain cations that can produce molten or aqueous sulfate salts, in presence of 0 to 250 part of water which must be controlled at 50 to 105 Celsius.

[Claim 2] A process according to claim 1 wherein: the ratio of acid to organic matter is between 0.1 to 20 or by adding concentrated sulfuric acid, must reach between 3 to 20.

[Claim 3] The process according to Claim 1 wherein: 0% up to 5% of common oxidants such as air, ozone, hydrogen peroxide, potassium permanganate or other oxidants, are used to oxidize and remove toxic and odorous substances, in the temperature range at 25 to 105 Celsius and acidic condition.

[Claim 4] The process according to Claim 1, which cations can be Magnesium, Ammonium, Iron, Manganese, Zinc, Copper, Aluminum and such cations which can produce molten soluble sulfate salts in various base forms such as oxide, carbonate, bicarbonate, sulfide or their mixture.

[Claim 5] The process according to claim 1, which all cations declared in claim 6 could be in metallic form and ammonia as gas state.

[Claim 6] The process according to claim 1, which by adding the one or more cations declared in claim 4, 5 in controlled conditions leads to the formation of two incompatible phases, such as the one section is organic phase and the other is aqueous solution or molten salt.

[Claim 7] The process according to claim 1, 6 by controlling of water content, which makes suitable difference in density range of 0.05 up to 0.7 g/ml of two phases declared in claim 6.

[Claim 8] The process according to claim 1, which reactor can be made of Plastic, stainless steel, glass-lined, rubber-lined, ceramic and cement.

[Claim 9] The process according to claim 1, which separation system can be made of decanter vessel or Any conventional device suitable for separating two liquids such as hydro cyclone.

Process according to all claims 1 to 9, in order to converting acid sludge to usable additive in bitumen and soluble sulfate salt which is useful in agriculture or some industries while the main feed of process is sludge byproduct of acid wash treatment of hydrocarbon based on sulfuric acid.

Fig.1

Block Flow Diagram for acid sludge recycling.

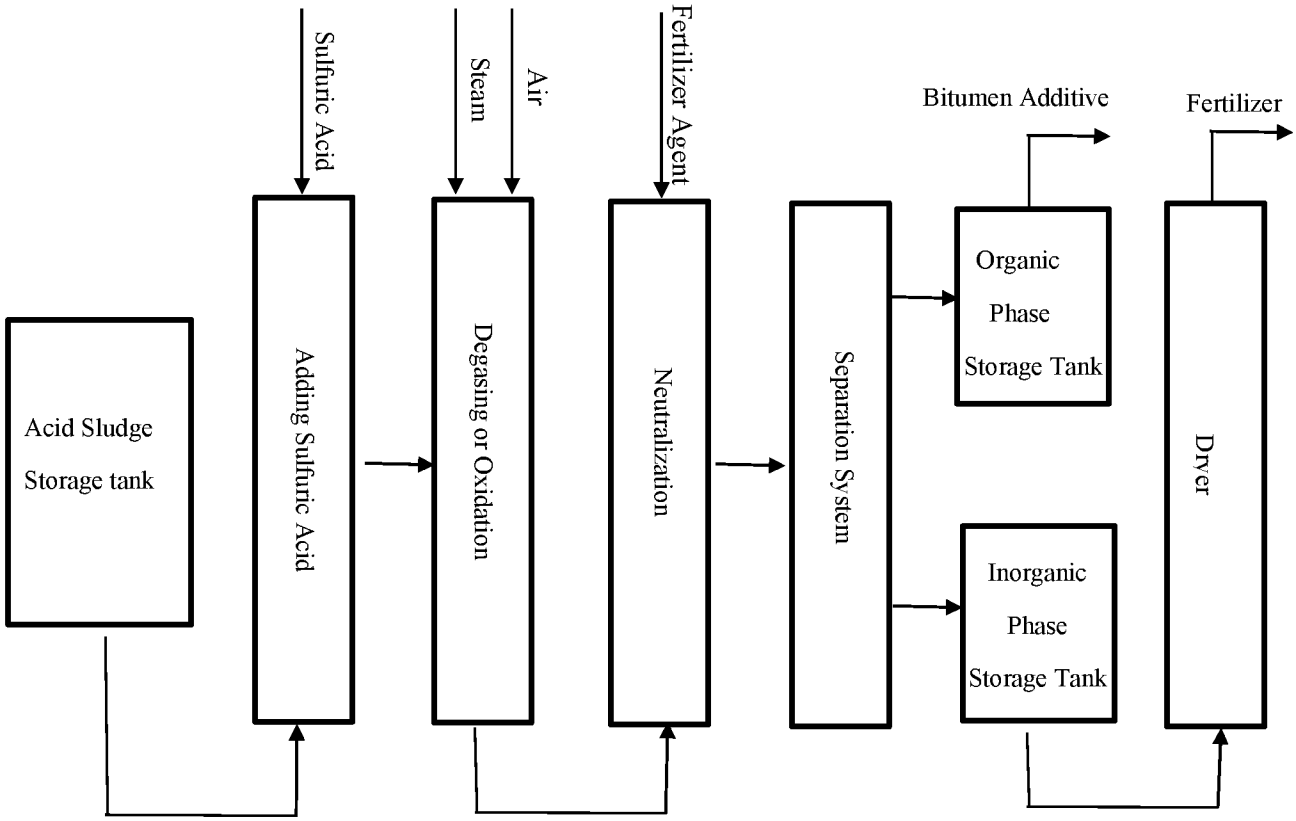
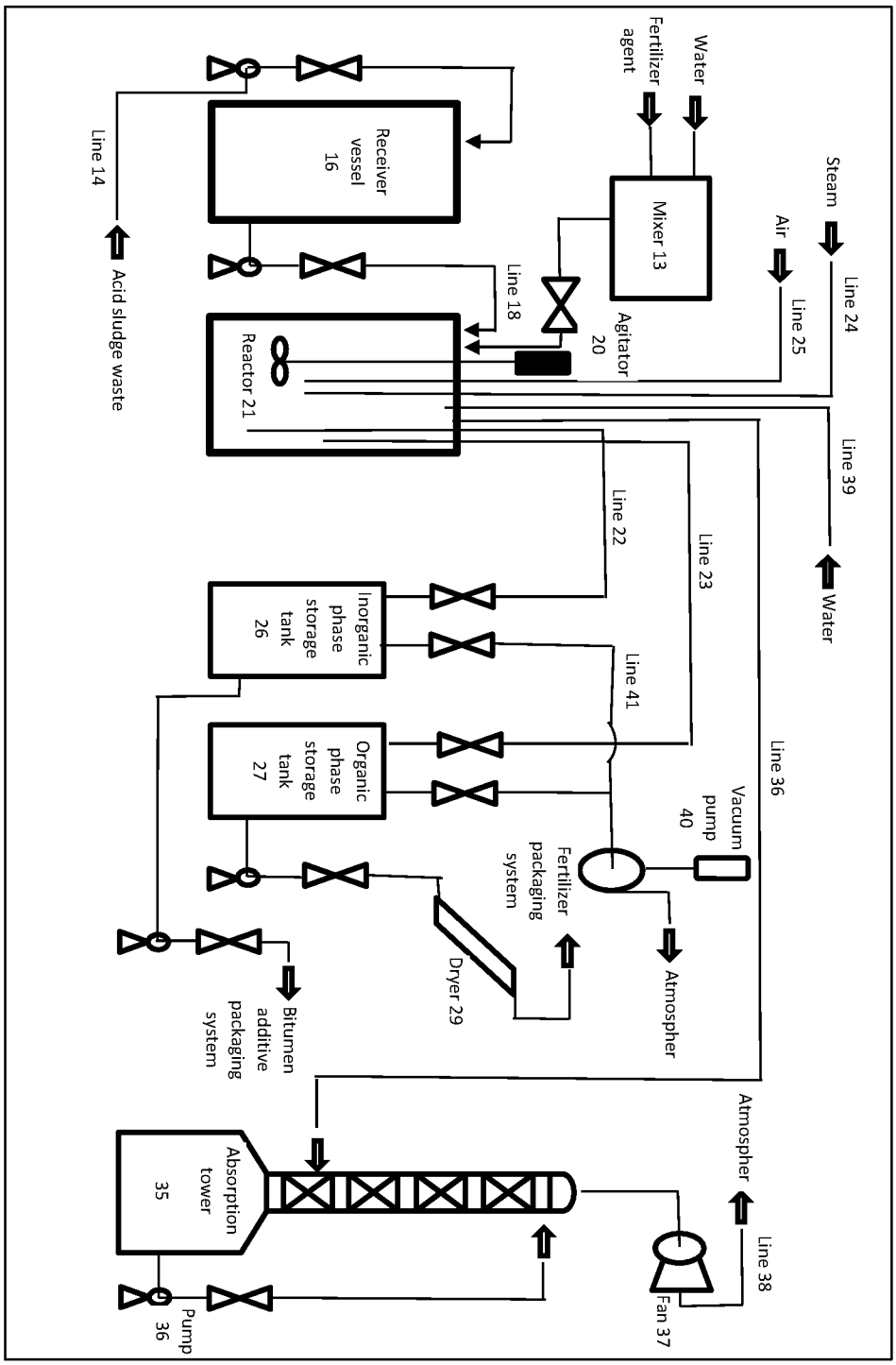


Fig.2

The work flow in flow chart for acid sludge recycling.



INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
C02F11/06,C02F1/20,C10G17/02 Version=2019.01

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B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C02F, C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

TotalPatent One, IPO Internal Database

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	B. ISLAM, "PETROLEUM SLUDGE, ITS TREATMENT AND DISPOSAL: A REVIEW ", Int. J. Chem. Sci.: 13(4), 2015, 1584-1602 the whole document	1-13
A	US5288392A (BENJAMIN S. SANTOS), 22 February 1994 the whole document	1-13
A	WO2014185957A1 (CIRIS ENERGY, INC.), 20 November 2014 the whole document	1-13

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
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Information on patent family members

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Citation	Pub.Date	Family	Pub.Date
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