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[Continued on next page]

(54) Title: PROCESS FOR RECOVERING HEAVY METALS FROM SOOT WATER

(57) Abstract: A process for recovering heavy metals, in particular vanadium, from a an aqueous suspension containing soot and ash particles, in particular from soot water obtained in the partial oxidation of hydrocarbons, by treating the suspension with ultrasound, filtering off the soot and ash particles, and precipitating the heavy metals from the filtrate by adjusting precipitation conditions.

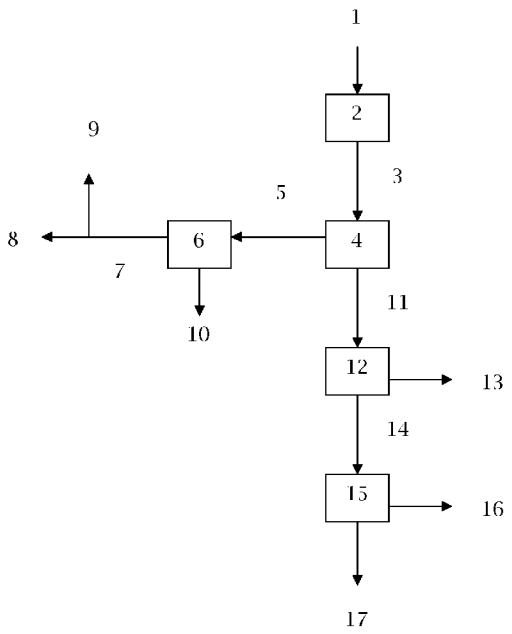

Fig. 1

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Process for Recovering Heavy Metals from Soot Water

Field of the Invention

This invention relates to a process for recovering heavy metals, in particular vanadium, from an aqueous suspension containing soot and ash particles, in particular from soot water obtained in the partial oxidation of hydrocarbons.

Prior art

In Ullmann`s Encyclopedia of Industrial Chemistry, 6th Edition, Volume 15, Chapt. 3.2.2, the Lurgi MPG® process for generating synthesis gas by partial oxidation of hydrocarbons, such as heavy oil, as well as the so-called MARS (Metals Ash Recovery System) process for the treatment of the aqueous suspension obtained when washing the synthesis gas, referred to as soot water and substantially containing soot and ash particles is described. The MARS process chiefly has the task of recovering the vanadium originating from the hydrocarbons used.

From among the heavy metals contained in the hydrocarbons used, chiefly iron, nickel and vanadium, the recovery of vanadium primarily is of economic interest.

The MARS process delivers a solid product rich in vanadium, which can be used in the metal production. For this purpose, the soot and ash particles are filtered out of the soot water and the retentate, the filter cake, is ashed in a multiple-hearth furnace to obtain the above-mentioned solid product rich in vanadium. The soot contained in the filter cake, which consists of carbon, serves as supplier of energy.

During ashing in the multiple-hearth furnace, as can be taken from EP 0 542 322 B1, an exact temperature control and adjustment of the oxygen partial pressure is required to avoid the conversion of these oxides into vanadium(V)

oxide (V_2O_5), since the same tends to form accretions in the furnace. However, the low process temperatures required according to EP 0 542 322 B1 lead to a slow course of the process and hence to large furnace dimensions and to a high content of carbon monoxide in the waste gas, which requires an expensive gas cleaning.

To consistently exploit the formation of carbon monoxide, the patent specification DE 101 52 686 B4 proposes to convert the soot obtained in the partial oxidation, which largely is carbon, into synthesis gas by adding oxygen and water. In this connection, two variants are described in this document.

In one variant, like in the MARS process, the procedure starts with a filter cake filtered out of soot water, which after having been dried is charged into an entrained-bed reactor, in which the soot present in the filter cake is converted into synthesis gas by adding oxygen and water. The solids present in the synthesis gas, which are loaded with vanadium, subsequently are separated from the gas.

In the other variant described in the patent specification DE 101 52 686 B4, the synthesis gas generated by partial oxidation is not washed with water. The soot and other solid constituents are separated from the gas in dry form and, by adding oxygen and water, charged into a soot gasification reactor, preferably in the form of steam. The solids loaded with vanadium are separated from the synthesis gas obtained.

The above-mentioned processes have the disadvantage that the very different valuable substances, namely soot and vanadium, which are contained in the solids mixture obtained as by-product of the partial oxidation, must be treated in a joint working step, whereby procedural compromises must be made, so that neither for soot nor for vanadium optimum processing conditions can be adjusted.

Therefore, it has been the object to provide a process for processing the solids mixture obtained in the partial oxidation, which provides for an optimum pro-

cessing each of soot and vanadium and a recovery of the vanadium as efficient as possible.

Description of the Invention

The object underlying the invention substantially is solved by the entirety of the features of claim 1. Further advantageous aspects of the process according to the invention can be found in the dependent claims.

In the process according to the invention it is provided to separate the heavy metals bound on or in the soot and ash particles, in particular vanadium, before the soot-ash mixture is treated further. Surprisingly, this is accomplished by a treatment of the suspension containing soot and ash particles, the so-called soot water, by treatment with ultrasound.

It has long since been known that superficial adhesions and substances bound to surfaces by adsorption, can be detached or desorbed by ultrasound. Ultrasound is known to be used for cleaning baths.

In the technical article by A. Profumo et al., Talanta 61 (2003), pp. 465-472, it is described how the type and extent of a nickel load in airborne dusts is measured. In doing so, the air is filtered and from the dust adhering to the filter nickel is separated by means of a multi-stage ultrasonic treatment. The work is, however, limited to the separation and succeeding analytical determination of nickel on filter dusts.

The dissertation Brüggemann, Freiberg, 2010, Chapt. 6.3.2, describes a method for the analytical determination of nickel, iron and vanadium adsorbed on solid gasification residues. To detach the metals from the residues, the residues are dispersed in water and treated with ultrasound, whereby the metals, at least in part, are separated from the residues. This paper also is directed to the analytical determination of various metal species, among other things vanadium.

Surprisingly, it was found that the separation of metals from gasification residues, which so far only is known from analytics, also is accomplished on a technical scale by means of ultrasonic treatment and thus can be used in an industrial process for the recovery of heavy metals, in particular vanadium, from residues of the partial oxidation. It is advantageous that most of the vanadium is transferred into a form which can be supplied to the metal recovery.

The process according to the invention for separating residues containing heavy metals, in particular vanadium, from the washing water loaded with soot and ash particles, which is obtained when washing raw synthesis gas, comprises the following process steps:

a) providing an aqueous suspension substantially containing soot and ash particles,
b) treating the suspension with ultrasound, wherein the adsorbed heavy metals bound on or in the suspended soot and ash particles, in particular vanadium, are at least partly converted into the aqueous phase,
c) separating the soot and ash particles depleted of heavy metals as retentate from the aqueous phase by means of a mechanical separation method,
d) precipitating the heavy metals, in particular the vanadium, from the filtrate by adjusting precipitation conditions,
e) thermal treatment of the retentate to obtain an ash containing heavy metals, in particular vanadium.

In a preferred embodiment of the process according to the invention it is intended to provide an aqueous suspension substantially containing soot and ash particles, which is obtained as soot water in the gasification or partial oxidation of hydrocarbons.

The ultrasonic treatment can be effected by ultrasonic generators mounted on the outside of the treatment vessel or immersed into the suspension. Ultrasonic generators mounted on the outside of the treatment vessel are preferred for reasons of cleaning and corrosion protection. By adjusting suitable pH values

in the aqueous phase, the transition of the heavy metals during the ultrasonic treatment can be further improved.

A preferred aspect of the invention is characterized in that the suspension first is thickened and the thickened sludge obtained thereby is treated according to process steps b) to e) from claim 1. The utilization of the introduced sound energy can be increased by this procedure.

Preferably, the separation of the soot and ash particles depleted of heavy metals is effected as retentate from the aqueous phase by means of filtration.

A further preferred aspect of the invention is characterized in that the thermal treatment of the retentate in process step e) is effected under gasification conditions. For this purpose, oxygen, air, oxygen-enriched air and/or water, preferably in the form of steam, is added to the retentate and a raw synthesis gas comprising carbon oxides and hydrogen is generated under gasification conditions. This procedure has the advantage that in the thermal processing of the retentate the soot is not merely processed to a cost-incurring waste gas, but to a usable raw synthesis gas. It is particularly advantageous to provide this configuration in the processing of soot water from the partial oxidation of hydrocarbons, since the raw synthesis gas obtained by gasifying the carbon-containing retentate can be processed further along with the synthesis gas obtained by the partial oxidation.

The ash containing heavy metals, which is obtained in process step e), can be dumped or recirculated. An advantageous aspect of the process according to the invention provides to at least partly recirculate this ash containing heavy metals to process step b), i.e. to the ultrasonic treatment. By combining the thermal treatment in process step e) and the new ultrasonic treatment in process step b), a further amount of heavy metals, for example of vanadium, is obtained in process step d). The heavy metal precipitate obtained in process step d) can be separated in a manner known to the skilled person and be further processed and subsequently be supplied to the dumping or metal recovery.

In principle, the precipitation of the dissolved heavy metals in process step d) can be effected in any way known to the skilled person; examples include the precipitation as metal hydroxides or metal sulfides by adding corresponding precipitating agents. What is also possible is the use of complex-forming precipitating agents such as EDTA. By corresponding adjustment of the pH value during the precipitation, the same can also be effected in a fractionated manner, so that different metals can be obtained as enriched fractions. The heavy-metal-containing, in particular vanadium-containing precipitate obtained subsequently can be used in the metal production.

In accordance with a further advantageous aspect, the process according to the invention also can be carried out such that the thermal treatment of the retentate in process step e) is effected under combustion or carbonization conditions, wherein advantageously a drying step is provided before the thermal treatment step.

Exemplary Embodiments

Further developments, advantages and possible applications of the invention can also be taken from the following description of exemplary embodiments and the drawings. All features described and/or illustrated form the invention per se or in any combination, independent of their inclusion in the claims or their back-reference.

In the drawings:

Fig. 1 shows a schematic representation of the process of the invention in accordance with a first embodiment,

Fig. 2 shows a schematic representation of the process of the invention in accordance with a second embodiment.

In the processes shown in Fig. 1 and Fig. 2, a suspension containing soot and ash particles is obtained as by-product in the partial oxidation of heavy oil according to the MPG® process. This suspension (1) also referred to as soot water

is charged into an ultrasonic treatment plant (2), in which the heavy metals bound on or in the suspended solid particles, in particular vanadium, are separated by means of ultrasound and are converted into the aqueous phase. The suspension (3) treated in this way is supplied to a filtration (4) in which the solid particles such as soot and ash particles are separated from the suspension as retentate (11). The filtrate (5), in which the dissolved heavy metals are contained, is charged into a precipitation stage (6) in which the heavy metals are separated from the aqueous phase as precipitate (10) by adding a suitable precipitating agent and possibly after adjusting a suitable pH value. The aqueous phase leaves the precipitation stage (6) as clear run (7) and is supplied to the waste water treatment (8) and/or guided back to the washing of the raw synthesis gas (9). The heavy-metal-containing or vanadium-containing precipitate (10) is charged to a further processing method, which is not subject-matter of the process according to the invention, and is processed therein such that it can be used as raw material in the metal production.

The retentate (11) containing soot and ash particles is charged as filter cake into a drying stage (12) and subsequently in the dried condition (14) into a thermal treatment plant (15). In the present example, the thermal treatment plant is configured as combustion. There, the retentate (14) is converted into a heavy-metal-containing or vanadium-containing ash (17), wherein the soot contained in the retentate is converted into waste gas (16). The waste gas (16) possibly is supplied to a waste gas treatment not shown in the Figure. The ash (17) can be used as raw material in the metal production. It can furthermore be recirculated to the ultrasonic treatment plant (2), in order to transfer a further amount of the heavy metals into the aqueous phase.

In the aspect of the invention as shown in Fig. 2, the suspension (1) first is charged into a thickening stage (18). The clear run (19) of the thickening stage is guided to a non-illustrated waste water treatment, stream (8'), and/or recirculated into the gas scrubber, stream (9'). The clear run of the thickening stage (19) can be treated together with the clear run (7) of the precipitation stage (6), as shown in Fig. 2, but a separate treatment also is possible. The thickened sludge (20) produced in the thickening stage (18) is charged into the ultrasonic

treatment plant (2), in which the heavy metals bound on or in the suspended solid particles, in particular vanadium, are separated by means of ultrasound and are converted into the aqueous phase. The suspension (3') treated in this way is supplied to a filtration (4) in which the solid particles such as soot and ash particles are separated from the suspension as retentate (11). From the filtrate (5), a precipitate (10) containing heavy metals is precipitated in the precipitation (6).

In contrast to the exemplary embodiment shown in Fig. 1, the retentate (11) containing soot and ash particles is not dried, but directly supplied to the thermal treatment (15') with the adhering residual moisture. Said thermal treatment is configured as gasification stage, in which the free carbon contained in the retentate (14) is partially oxidized by adding oxygen (22) and water (21), preferably as steam, to obtain a raw synthesis gas chiefly containing carbon monoxide and hydrogen. It is advantageous that the added amount of water, due to the residual moisture of the retentate, can be reduced, whereby the energy consumption of the process for evaporating the water and for overheating the steam is decreased. At the same time, the remaining solids content is converted into a heavy-metal-containing ash in the gasification stage (15'). The mixture of raw synthesis gas and ash (23) is charged into a solids separator (24), in which the raw synthesis gas (25) is separated from the ash (17). Optionally, the ash can wholly or preferably in part be recirculated to the ultrasonic treatment (2) (not shown in Fig. 2) and pass through the same once more, so that a further amount of the heavy metals is transferred into the aqueous phase and subsequently recovered by precipitation. The raw synthesis gas (25) is combined with the raw synthesis gas from the partial oxidation of heavy oil and processed further along with the same. The further processing steps include the process stages known to the skilled person, such as the CO conversion, the synthesis gas scrubbing, for example by the Rectisol® process, for removing acid gas constituents, and the pressure swing adsorption for separating a fraction rich in hydrogen from the synthesis gas.

Industrial Applicability

The invention thus provides a process which in a simple way provides for recovering the heavy metals obtained with the ash in the partial oxidation of hydrocarbons, for example in the gasification of heavy oil, in particular the vanadium esteemed in the production of stainless steels, as enriched fraction. Due to the use of ultrasound for promoting the transition of the heavy metals from the soot or ash particles into the aqueous phase, it is accomplished to carry out the process according to the invention with a lower energy consumption and a reduced use of aggressive chemicals than is the case in processes already known in the prior art.

List of Reference Numerals

(1)	suspension (also referred to as soot water)
(2)	ultrasonic treatment plant
(3, 3')	treated suspension, treated thickened sludge
(4)	filtration
(5)	filtrate
(6)	precipitation stage
(7)	clear run of the precipitation stage
(8, 8')	clear run to the waste water treatment
(9, 9')	clear run to the scrubber of the raw synthesis gas
(10)	precipitate containing heavy metals
(11)	retentate
(12)	drying stage
(13)	retentate (filter cake), moist
(14)	retentate (filter cake), dried
(15, 15')	thermal treatment plant
(16)	waste gas
(17)	ash, containing heavy metals
(18)	thickening stage
(19)	clear run of the thickening stage
(20)	thickened sludge
(21)	addition of water
(22)	addition of oxygen
(23)	ash-containing raw synthesis gas
(24)	solids separator
(25)	raw synthesis gas

Claims:

1. A process for recovering heavy metals, in particular vanadium, from aqueous suspensions containing soot and ash particles, wherein the heavy metals are bound on or in the soot and ash particles, comprising the following process steps:

   a) providing an aqueous suspension substantially containing soot and ash particles,

   b) treating the suspension with ultrasound, wherein the adsorbed heavy metals bound on or in the suspended soot and ash particles, in particular vanadium, are at least partly converted into the aqueous phase,

   c) separating the soot and ash particles depleted of heavy metals as retentate from the aqueous phase by means of a mechanical separation method,

   d) precipitating the heavy metals, in particular the vanadium, from the filtrate by adjusting precipitation conditions, and recovering a precipitate containing heavy metals,

   e) thermal treatment of the retentate to obtain an ash containing heavy metals, in particular vanadium.

2. The process according to claim 1, characterized in that the aqueous suspension substantially containing soot and ash particles is obtained as soot water in the partial oxidation of hydrocarbons.

3. The process according to claim 1 or 2, wherein the suspension first is thickened and the thickened sludge obtained thereby is treated according to process steps b) to e) from claim 1.

4. The process according to claims 1 to 3, characterized in that the separation of the soot and ash particles depleted of heavy metals as retentate from the aqueous phase is effected by means of filtration.

5. The process according to any of the preceding claims, characterized in that the thermal treatment of the retentate in process step e) is effected under gasification conditions, wherein a raw synthesis gas is obtained.

6. The process according to claims 2 and 5, characterized in that the raw synthesis gas obtained by gasification of the retentate is processed further along with the synthesis gas obtained in the partial oxidation of hydrocarbons.

7. The process according to any of the preceding claims, characterized in that the heavy-metal-containing ash obtained in process step e) is at least partly recirculated to process step b).

8. The process according to claims 1 to 4, characterized in that the thermal treatment of the retentate in process step e) is effected under combustion or carbonization conditions, wherein a drying step is provided before the thermal treatment step.

9. A heavy-metal-containing, in particular vanadium-containing precipitate, obtainable by a process according to claims 1 to 8.

10. Use of the heavy-metal-containing, in particular vanadium-containing precipitate according to claim 9 for metal production.

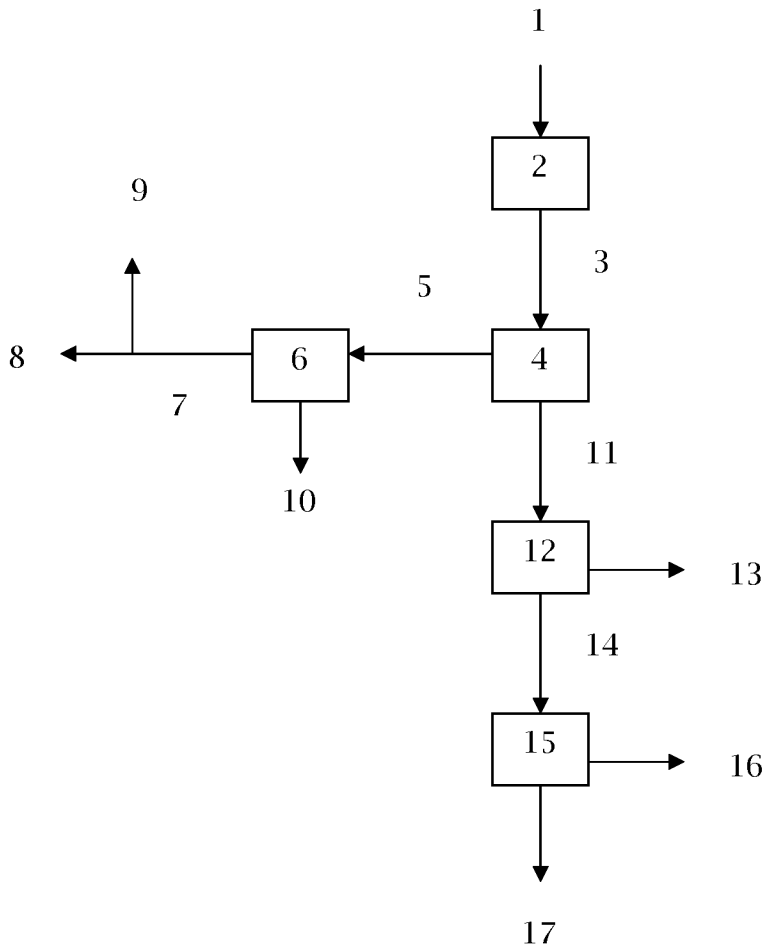

Fig. 1

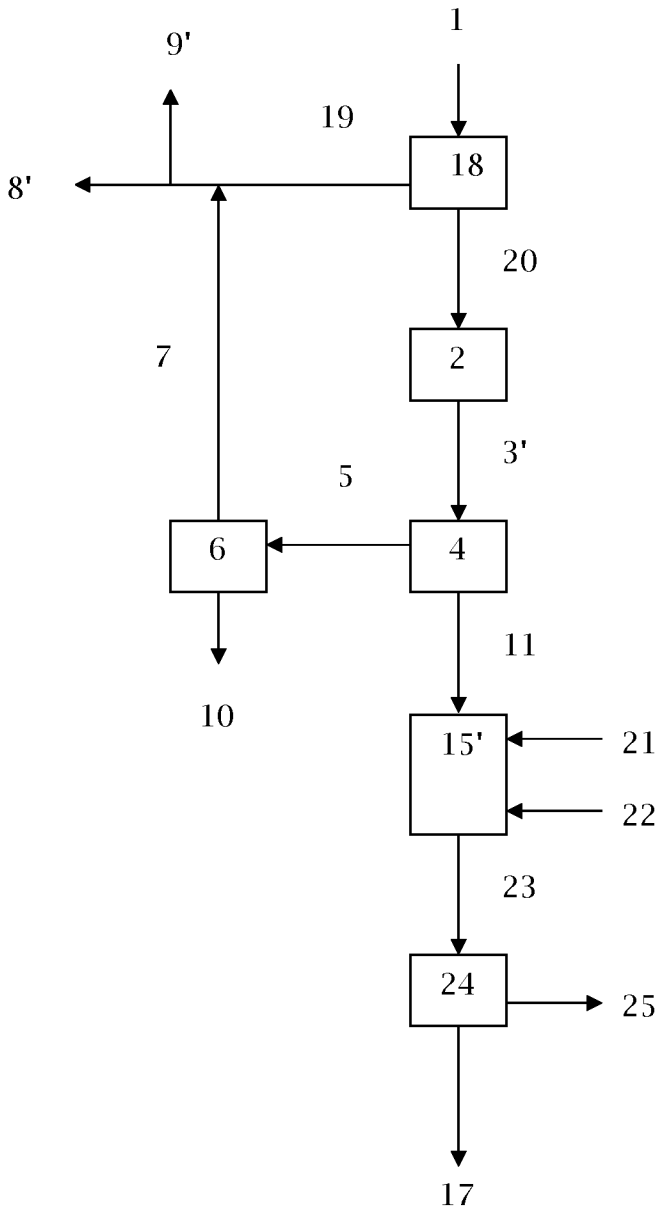

Fig. 2

INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER
INV. C22B7/00 C22B7/02 C22B34/22
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C22B

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)
EPO-Internal, COMPENDEX, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 8 337408 A (TOKYO ELECTRIC POWER CO; KAIJO KK; NIPPON HYOMEN KAGAKU KK; ART CERAMI) 24 December 1996 (1996-12-24) the whole document	1-10
X	US 4 100 251 A (REINHARDT NILS ET AL) 11 July 1978 (1978-07-11)	9,10
A	the whole document	1-8

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"P" document published prior to the international filing date but later than the priority date claimed

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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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Date of the actual completion of the international search	Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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