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(54) Title: METHOD FOR REPROCESSING GAS CONDENSATE

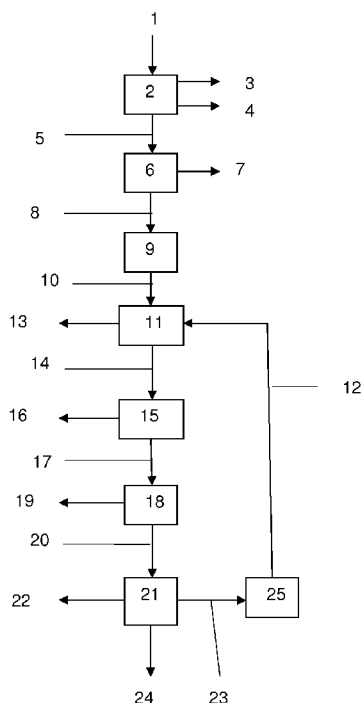


Fig. 1

(57) Abstract: A method for reprocessing a gas condensate which has been separated from raw synthesis gas produced by gasification of coke or coal in a fixed-bed pressure gasification reactor, for the further treatment, comprising the following method steps carried out one after the other: - separation of oils and tar by mechanical methods, - adjustment of the pH value of the gas condensate by absorption of sour gas obtained process-internally, - extraction of the phenols from the gas condensate by a solvent, - separation of ammonia and, separately, of a sour gas chiefly consisting of H₂S and CO₂ in a physical way, wherein the absorption of the sour gas is carried out under elevated pressure and the gas condensate subsequently is depressurized to the pressure existing in the extraction.



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TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU,
TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE,
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Method for Reprocessing Gas Condensate

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Field of the Invention

This invention relates to a method for reprocessing a gas condensate which has been separated from raw synthesis gas produced by gasification of coke or coal in a fixed-bed pressure gasification reactor, for the further treatment, comprising the following method steps carried out one after the other:

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- separation of oils, tar and dust by mechanical methods,
- adjustment of the pH value of the gas condensate
- extraction of the phenols from the gas condensate by a solvent,
- 20 - separation of ammonia and, separately, of a sour gas chiefly consisting of H_2S and CO_2 in a physical way.

Prior art

By means of fixed-bed pressure gasification reactors solid fuel, such as coal, coke or other carbonaceous fuel, is gasified with steam and oxygen as gasification medium at elevated temperature and, in most cases, under overpressure to obtain a synthesis gas containing carbon monoxide and hydrogen, wherein a solid ash is obtained, which is discharged from the reactor via an ash discharge grate which in many cases is formed as rotary grate. This type of reactor frequently also is referred to as FBDB (= Fixed Bed Dry Bottom) pressure gasifier.

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When cooling synthesis gas obtained by the gasification of carbonaceous solids, a carbonaceous waste water referred to as gas condensate is obtained. Before the gas condensate can be disposed of as waste water in a biological clarification plant, it must be reprocessed for reasons of environmental protection. In doing so,
5 oils, tar and dust as well as phenols, ammonia and a so-called sour gas chiefly consisting of carbon dioxide and hydrogen sulfide are separated from the gas condensate.

When reprocessing the gas condensate, solids such as tar and dust as well as oil
10 first are separated mechanically. The greatest part of these constituents is separated in a settling tank called tar separator by mechanical separation methods, for example by sedimentation. Fine cleaning subsequently is effected by filtration, cf. Ullmann's Encyclopedia of Industrial Chemistry, Sixth Edition, Vol. 15, p. 369 and p. 437, Fig. 75.

15 As next reprocessing step the separation of the phenols is carried out. This can be effected by an extraction process, such as the Lurgi Phenosolvan process, cf. Ullmann's Encyclopedia of Industrial Chemistry, Sixth Edition, Vol. 15, p. 433. The use of extractors of the mixer-settler type has proved successful. As extracting
20 agent diisopropyl ether frequently is used, and alternatively butyl acetate and methylisobutyl ketone can also be used.

The Phenosolvan process proceeds continuously, with the extracting agent being circulated. It is liberated from its phenol load by distillation. After passing through
25 the extraction step, the gas condensate as refined product is liberated from extracting agent residues by stripping e.g. with oxygen.

The extraction of the phenols, i.e. phenols passing over from the gas condensate into the extracting agent, is effected the more effectively the smaller the degree of
30 dissociation of the phenols in the gas condensate. Since phenols react acidic in aqueous solution, but due to its ammonia content the gas condensate has a basic pH value of typically 9 to 10, the degree of dissociation of the phenols is

comparatively high, whereby the effectiveness of the extraction is reduced. To effectively carry out the extraction of the phenols, the pH value of the gas condensate must be adjusted to a suitable value in dependence on the extracting agent used.

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From the Chinese Patent Applications CN 102241453 A and CN 102674608 A it is known that lowering the pH value of the gas condensate can be effected by absorption of sour gas. Since this absorption is a process proceeding slowly, large and hence expensive tanks, such as absorption columns of correspondingly large design, are required.

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After the separation of the phenols, hydrogen sulfide, carbon dioxide and ammonia still are to be separated from the gas condensate. For this task, for example, the so-called Chemie Linz-Lurgi (CLL) process can be used, cf. Ullmann's Encyclopedia of Industrial Chemistry, Sixth Edition, Vol. 15, p. 435. The separation here is effected in a physical way, by stripping with steam, and by distillation. In one process step, hydrogen sulfide and carbon dioxide are jointly removed by distillation, as so-called sour gas. In a separate process step, ammonia is separated from the gas condensate by distillation and stripping.

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It is the object of the present invention to provide an improved method for separating phenols, sour gas and ammonia from gas condensate, which can do with small dimensions of the pipe conduits and apparatuses used, whereby the investment costs are kept low.

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Description of the Invention

This object is solved by a method for reprocessing a gas condensate which has been separated from raw synthesis gas produced by gasification of coke or coal in a fixed-bed pressure gasification reactor, for the further treatment, comprising the following method steps carried out one after the other:

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(a) separation of oils and tar by mechanical methods,

(b) adjustment of the pH value of the gas condensate by absorption of sour gas separated from the gas condensate in step (d),

(c) extraction of the phenols from the gas condensate,

5 (d) separation of ammonia and, separately, of a sour gas chiefly consisting of H₂S and CO₂ in a physical way, and at least partly recirculating the sour gas for use in step (b);

characterized in that the absorption in step (b) is carried out under elevated pressure and the gas condensate subsequently is depressurized to the pressure existing in the extraction of step (b).

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According to the invention, the absorption of the sour gas is carried out under overpressure, as under this condition the absorption of gases such as CO₂ and H₂S in the gas condensate is effected more quickly, whereby a shorter residence time and hence a smaller overall size of the absorption means is required.

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Preferred Aspects of the Invention

As absorption means absorption columns have proved successful, which if necessary can be equipped with internal fittings and/or packings, in order to intensify the contact between the gas condensate and the sour gas.

20

After performing the absorption, the gas condensate is depressurized to the pressure at which the extraction is carried out. The extraction frequently is carried out at atmospheric pressure.

25 The depressurization can be carried out either in a separate tank or in the first fixing chamber of the mixer-settler in flow direction of the gas condensate. With the depressurization in the mixer-settler, the separate expansion tank is saved. It is, however, only possible when the gas evolution during the depressurization is limited such that the operation of the mixer-settler is not impaired.

30

It is particularly advantageous when the absorption is carried out in the pressure range of 1.5 to 10 bar. This range constitutes the optimum compromise between

the increased effectiveness of the absorption due to the overpressure and the equipment expenditure for pressure increase.

For the effectiveness of the phenol extraction process it is particularly advantageous to adjust the pH value of the gas condensate by means of the absorption of the sour gas such that after the depressurization it preferably is at least 6.5 and not more than 8.5 or most preferably at least 7.8 and not more than 8.2. In these preferred or most preferred ranges, by far the largest part of the phenols is neutralized and thus can be removed from the gas condensate with high effectiveness by the downstream phenol removal process. On the other hand, the pH value is large enough to keep the acid corrosion on apparatuses and pipe conduits low.

Another advantageous aspect of the invention consists in using diisopropyl ether or alternatively butyl acetate or methylisobutyl ketone as solvents for the extraction of the phenols.

Exemplary Embodiments

Further developments, advantages and possible applications of the invention can also be taken from the following description of non-limiting exemplary embodiments and numerical examples as well as the drawing. 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.

With reference to the drawing, Fig. 1, the invention will now be explained in detail.

Fig. 1 shows an exemplary method flow diagram of the inventive reprocessing of gas condensate separated from synthesis gas produced in a fixed-bed pressure gasification reactor for the treatment in a biological clarification plant.

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The gas condensate 1 separated from the raw synthesis gas in a condensation means downstream of a fixed-bed pressure gasification reactor, cooled to 80 °C

and depressurized to ambient pressure is introduced into a settling tank 2 referred to as tar separator. By phase separation and sedimentation, an oil phase 3 and a tar and dust phase 4 here are separated from the gas condensate 1. The gas condensate 5 prepurified in this way is introduced into a filter system 6, in which a residual phase 7 consisting of fine dust particles, oil and tar is separated from the gas condensate. The gas condensate 8 then is introduced into a pressure increasing means 9 and brought to a pressure of 5 bar. The gas condensate 10 treated in this way is introduced into an absorption means 11 in which it is brought in contact with sour gas 12. As absorption means, an absorption column is used.

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The sour gas 12 chiefly consisting of carbon dioxide and hydrogen sulfide for one part is absorbed by the gas condensate 10, for the other part 13 discharged from the absorption means, and supplied to the further treatment (not shown). Due to the absorption of the sour gas, the pH value of the gas condensate is lowered from 9 to 8. The gas condensate 14 treated in this way is introduced into a depressurizing means 15. Here, it is depressurized to atmospheric pressure, at which the succeeding phenol extraction is carried out in the mixer-settler. The gas 16 released during depressurization is supplied to the waste disposal (not shown). The gas condensate 17 treated in this way subsequently is introduced into an extraction plant 18 for separating the phenols. Here, the gas condensate is brought in contact with a suitable extracting agent, with the phenols passing over from the gas condensate into the extracting agent. The extraction is carried out in an extraction plant of the mixer-settler type. As extracting agent diisopropyl ether is used. The phenols are absorbed the better by the extracting agent used, the less they are dissociated, which is why the degree of dissociation of the phenols has been reduced by the preceding decrease of the pH value. Within the extraction plant 18 a phenol phase 19 is separated from the extracting agent by distillation and passed over to the further treatment (not shown). Within the extraction plant 18, by stripping with nitrogen, extracting agent residues are separated from the gas condensate liberated from phenols and added to the extracting agent circulating within the extraction plant 18.

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The dephenolized gas condensate 20 then is passed over to a plant 21 operating by the CLL process, for separating ammonia and sour gas. Here, first ammonia and then the so-called sour gas 23 chiefly consisting of carbon dioxide and hydrogen sulfide is stripped out of the gas condensate at atmospheric pressure by means of steam in separate steps. The separated ammonia 22 is passed over to the further treatment (not shown). The gas condensate 24 now is reprocessed to such an extent that it can be transferred into a biological clarification plant (not shown). The sour gas 23 leaves the CLL plant 21 with 4 bar and in a pressure increasing means 25 is brought to the pressure existing in the absorption means 11, in this case 5 bar, and introduced into the absorption means 11 as sour gas stream 12, in order to lower the pH value of the gas condensate.

Industrial Applicability

The invention improves the economy of the method for reprocessing gas condensate in that it provides for smaller overall sizes for the absorption means serving for the absorption of sour gas, and hence for the adjustment of the pH value.

List of Reference Numerals

	1	gas condensate
	2	settling tank
5	3	oil phase
	4	tar and dust phase
	5	gas condensate
	6	filter system
	7	tar and dust phase
10	8	gas condensate
	9	pressure increasing means
	10	gas condensate
	11	absorption means
	12	sour gas
15	13	sour gas
	14	gas condensate
	15	depressurizing means
	16	sour gas
	17	gas condensate
20	18	extraction plant for phenol separation
	19	phenol phase
	20	gas condensate
	21	plant for separating ammonia and sour gas (CLL process)
	22	ammonia
25	23	sour gas
	24	gas condensate
	25	pressure increasing means

Claims:

1. A method for reprocessing a gas condensate which has been separated from raw synthesis gas produced by gasification of coke or coal in a fixed-bed pressure gasification reactor, for the further treatment, comprising the following method steps carried out one after the other:
 - (a) separation of oils and tar by mechanical methods,
 - (b) adjustment of the pH value of the gas condensate by absorption of sour gas separated from the gas condensate in step (d),
 - 10 (c) extraction of the phenols from the gas condensate,
 - (d) separation of ammonia and, separately, of a sour gas chiefly consisting of H_2S and CO_2 in a physical way and at least partly recirculating the sour gas for use in step (b);

characterized in that the absorption in step (b) is carried out under elevated pressure and the gas condensate subsequently is depressurized to the pressure existing in the extraction of step (b).
2. The method according to claim 1, **characterized in that** the absorption carried out in step (b) of claim 1 is carried out in an absorption column.
3. The method according to any of the preceding claims, **characterized in that** the depressurization of the gas condensate is carried out in a separate expansion tank.
- 20 4. The method according to any of the preceding claims, **characterized in that** for carrying out the extraction in step (c) a mixer-settler comprising at least one mixing chamber is used.
- 25 5. The method according to any of the preceding claims, **characterized in that** the depressurization of the gas condensate is carried out in the first mixing chamber of the mixer-settler in flow direction of the gas condensate.
6. The method according to any of the preceding claims, **characterized in that** the absorption in step (b) is carried out at a pressure of at least 1.5 and not more than 10 bar.
- 30

7. The method according to any of the preceding claims, **characterized in that** after the depressurization the pH value of the gas condensate is at least 6.5 and not more than 8.5.
8. The method according to any of the preceding claims, **characterized in that** after the depressurization the pH value of the gas condensate is at least 7.8 and not more than 8.2.
9. The method according to any of the preceding claims, **characterized in that** as extracting agent in step (c) of claim 1 there is alternatively used diisopropyl ether, butyl acetate or methylisobutyl ketone.

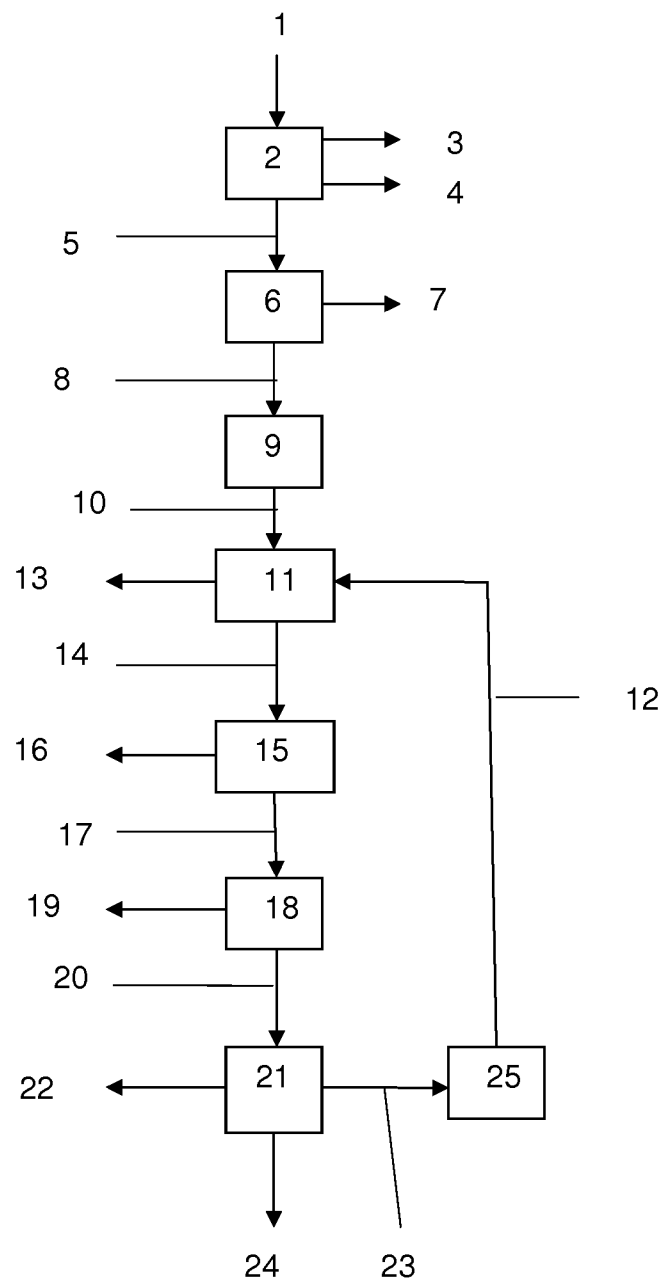


Fig. 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/076488

A. CLASSIFICATION OF SUBJECT MATTER

INV. C10K1/00 C10K1/04 C10J3/20 C02F9/00
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)

C10K C10J C02F

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, 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	US 4 097 539 A (STONNER HANS-MARTIN ET AL) 27 June 1978 (1978-06-27) figure 1 column 3 - column 4 -----	1-9
A	CN 102 241 453 A (UNIV ZHONGKAI AGRI & ENG) 16 November 2011 (2011-11-16) cited in the application figure 1 the whole document -----	1-9
A	US 3 711 402 A (ZUMBRUNN J ET AL) 16 January 1973 (1973-01-16) example 1 -----	1-9



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

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

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"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

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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