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(54) **Selenodemercuration of natural gas condensates.**

(57) A process for the removal of mercury from natural gas condensate wherein the natural gas condensate is contacted with elemental selenium in a reactor vessel. A highly dispersed form of selenium is also disclosed.

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SELENODEMERCURATION OF NATURAL GAS CONDENSATES

The present application is directed to a process for the removal of impurities from natural gas condensate, and particularly, to a process for the removal of mercury from natural gas condensate.

Natural gas which is produced from a natural gas well is typically separated into components, which are in turn purified to provide products for a variety of end uses. The high-pressure mixture produced from the well, i.e., the wellstream, is typically sent to a separator vessel or a series of separator vessels maintained at progressively lower pressures where the wellstream is separated into a gaseous fraction and a liquid fraction.

The gaseous fraction leaving the separator, which may contain the impurities mercury, carbon dioxide and hydrogen sulfide, is sent to a gas treatment and purification plant where typically the mercury concentration is reduced to, 0.1 micrograms/m^3, the CO_2 concentration is reduced to the parts per million (ppm) level, and the H_2S to about one (1) ppm.

The liquid fraction is typically preheated to effect partial vaporization and is then separated, for example, in a stabilizer column. In the upper section of the stabilizer column, the stream is rectified, i.e., the heavy hydrocarbons are removed from the vapor phase, and in the lower section of the stabilizer column, the liquid stream is stripped of its light hydrocarbon components. Complete stabilization can be further enhanced by heating the bottom liquid stream of the stabilizer column in a reboiler. The reboiler supplies additional heat in order to reduce the light hydrocarbon content of the liquid. The stabilizer column produces two streams, a stream which leaves the top of the stabilizer column containing low molecular weight hydrocarbons e.g., C_1-C_4, and other gases, and a stabilized condensate stream which leaves the bottom of the stabilizer column.

It has been found that the mercury in wellstreams from gas producing wells which contain mercury is partitioned among the gaseous and liquid streams. This mercury is thought to originate from the geologic deposits in which the natural gas is entrapped.

Typical steps for the processing of the liquid fraction of the wellstream do not reduce the amount of mercury in the liquid fractions leaving the separator. For example, in the production of ethylene, a natural gas condensate is commonly passed through a heat exchanger constructed of aluminium. Such equipment exists in the section of the ethylene manufacturing facilities where ethylene is separated from hydrogen, ethane and other hydrocarbons by chilling. It has been found that mercury tends to amalgamate with the aluminium of which the heat exchanger is constructed thereby creating the risk of corrosion cracking with potentially catastrophic results.

The present invention minimizes the potential risk of mercury damage to expensive downstream processing equipment by reducing the amount of mercury in the natural gas condensate. The present invention comprises a process for the removal of mercury from natural gas condensate wherein the natural gas condensate is contacted with elemental selenium. The present invention minimizes the risk of equipment failure by providing a process for the removal of mercury from natural gas condensates.

In order to minimize the potential damage to expensive processing equipment which may result from the processing of natural gas condensate containing high levels of mercury, the present invention provides a simple process for removing mercury from natural gas condensate. It has been found that the amount of mercury in a natural gas condensate can be substantially reduced by the process of the present invention which comprises passing the condensate into a reactor containing elemental selenium, preferably at a temperature of about 15 °C to about 217 °C, the melting point of selenium.

In practising the present invention, the elemental selenium may be in the form of pellets having a sufficiently small diameter so as to expose a large surface area of the selenium to the condensate without causing untolerable resistance to flow creating significant back pressure.

Alternatively, the elemental selenium may be in a highly dispersed form. As used herein, the term "highly dispersed form" refers to selenium which has been deposited on an inert carrier by evaporation of a solution of selenium in a solvent, or other deposition techniques, such as by vapor deposition, to provide a deposit of the selenium on the carrier. For example, a solution of elemental selenium may be prepared by dissolving the selenium in carbon disulfide (CS_2) or ether. The selenium/carbon disulfide or ether solution is mixed with a porous solid such as alumina extrudate having a large surface area such as 180m^2 per gram and a large pore size, e.g., 40 - 100 Angstroms (400 to 1000nm), to form a slurry. By evaporating the carbon disulfide or ether while continuously stirring the slurry, the selenium will be deposited in a highly dispersed form on the solid. This process may be repeated to increase the selenium content of the solid.

The solid can be any suitable solid for the

forming of an inert carrier, for example alumina, zirconia, silica-alumina, carbon, etc. Suitable solids typically have large surface areas, e.g., 200 square meters per gram, and large pores, preferably at least about 20 angstroms.

Steps (i) - (iv) exemplify the steps of one method for preparing highly dispersed selenium.

(i) A solution of elemental selenium is prepared by dissolving 0.05 grams of elemental selenium in 100 grams of CS_2.

(ii) The solution is then mixed with 100 grams of a porous solid such as alumina 1/16" (0.159cm) extrudate which has a large surface area and large pore size to form a slurry.

(iii) CS_2 contained in the slurry prepared in step (ii) is allowed to evaporate while the slurry is continuously stirred. Residual CS_2 may be removed by the application of a vacuum.

(iv) After all the CS_2 is removes in step (iii), the solid which now contains highly dispersed selenium is ready for use in selenodemercuration of natural gas condensate.

(v) Steps (i) - (iv) may be repeated to increase the selenium content of the solid.

In practising the process of the present invention, the selenium is placed in a conventional reactor, such as a carbon steel reactor, and the natural gas condensate is fed into the reactor and allowed to flow over the selenium. The mercury in the condensate reacts with the selenium according to the following formula:

$Se + Hg \rightarrow HgSe$

It is believed that the mercuric selenide, which is not soluble in the condensate, remains with the selenium on the pellets or on the inert carrier.

In the event that some of the mercuric selenide remains in or is dislodged into the condensage, a filter capable of removing mercuric selenide may be disposed downstream of the reactor. for example, the filter may have holes of about 1/2 micron, however, it will be appreciated by those skilled in the art that any filtering technique capable of filtering out the mercuric selenide will be suitable.

The present invention advantageously operates successfully over a range of temperatures and presures. The pressure in the reactor can be set from about 1 to 40 atmospheres (101 KPa to 4050 KPa) and is preferably from about 10 to 15 atmospheres (1010 KPa to 1520 KPa). The temperature in the reactor can range from about 15° C -217° C, and is most preferably about 125 - 175° C. The space velocity, i.e., the volume of liquid flowing through the reactor every hour divided by the volume of solid, is preferably kept below about 20.

The stream leaving the reactor contains the condensate with a reduced amount of mercury.

The process of the present invention has been successful in reducing the amount of mercury in natural gas condensate from above about 1100 ppb to below about 20 ppb. It will be appreciated by those in the art that the mercury content of the natural gas condensate can be determined by conventional methods, such as ASTM method D-3323.

The following examples will further illustrate the present invention.

Example 1

a) About 4ml (3.77gm) of selenium pellets having an average diameter of about 4mm. were placed in a steel reactor equipped with means for temperature and pressure control, pumps, and a recovery system.

b) Condensate with a Hg content of 1100 ppb was introduced into the reactor at atmospheric pressure and a temperature of 125° C at a rate of 16ml/hour.

c) The treated condensate leaving the reactor, after the application of this treatment, had a mercury content of 114 ppb which shows 90% Hg removal.

Example 2

Example 1 was repeated at a temperature of 160° C. The treated condensate leaving the reactor had a mercury content of 33 ppb, which shows 97% Hg removal.

Example 3

Example 1 was repeated with the same reactor but without the the selenium. The condensate, after the application of this treatment, had a mercury content of 1100 ppb indicating no Hg removal in the absence of selenium.

Example 4

Example 2 was repeated with the same reactor but without the selenium. Again the condensate, after the application of this treatment, had a mercury content of 1100 ppb indicating no Hg removal in the absence of selenium.

Examples 1 and 2 demonstrate that the present invention is capable of reducing the mercury content by at least 90%. Example 3 and 4 demonstrate that heating and contacting the condensate with the steel reactor, without the elemental Se, will not

reduce the mercury content of the condensate.

Claims

1. A process for the removal of mercury from natural gas condensate comprising the step of: contacting said natural gas condensate with elemental selenium in a reactor vessel.
2. A process according to claim 1 wherein said reactor vessel is maintained at a temperature of about 15 - 215° C.
3. A process according to claim 1 or 2, wherein said reactor vessel is maintained at a pressure of substantially 1 to 40 atmospheres (101 to 4050 KPa).
4. A process according to claim 1, 2 or 3, wherein said elemental selenium is in the form of pellets.
5. A process according to claim 4, wherein said pellets have an average diameter of substantially 1 to 10 mm.
6. A process according to claim 4, wherein said pellets have an average diameter of substantially 3 to 5 mm.
7. A process according to any preceding claim wherein said reactor vessel is maintained at a temperature of substantially 125 -160° C.
8. A process according to any preceding claim wherein the space velocity is below substantially 20.
9. A process according to any preceding claim wherein said selenium is in highly dispersed form.
10. A process according to claim 9 wherein said selenium is dispersed on an alumina carrier.
11. A highly dispersed form of selenium comprising elemental selenium deposited on an inert carrier.
12. A highly dispersed form of selenium according to claim 11 wherein said carrier comprises alumina.
13. A highly dispersed form of selenium according to claim 11 wherein said carrier comprises silica-alumina.

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EUROPEAN SEARCH REPORT

Application Number

EP 90 31 2001

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	US-A-4 880 527 (AUDEH) * Claims 1,2 *	1	C 10 G 25/00
A	JP-A-5 007 599 (MITSUI MINING SMELT) * Abstract *	1	
P,A	EP-A-0 357 873 (JGC CORP.) * Claim 1; page 2, lines 4-15 *	1	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C 10 G

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	22 January 91	DE HERDT O.C.E.

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
Y: particularly relevant if combined with another document of the same catagory
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention

E: earlier patent document, but published on, or after the filing date
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