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(71) Applicant: SHELL OIL COMPANY [US/US]; Intellectual Property, P.O. Box 2463, 900 Louisiana, Houston, TX 77252-2463 (US).

(72) Inventor: UNGER, Phillip, Edward; 10 Shadow Lane, Houston, TX 77080 (US).

(74) Agents: HADLOCK, Timothy, J. et al.; Shell Oil Company, Intellectual Property, P.O. Box 2463, 900 Louisiana, Houston, TX 77252-2463 (US).

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(54) Title: METHOD OF REDUCING HALIDES IN SYNTHESIS GAS

(57) Abstract

The invention is a method for reducing halide content of a synthesis gas stream by mixing a metal compound of potassium oxide, potassium hydroxide, potassium bicarbonate, potassium carbonate, sodium oxide, sodium hydroxide, sodium bicarbonate, or sodium carbonate, with a carbonaceous feed material which contains halide-containing compounds; gasifying the carbonaceous feed material in an entrained flow gasifier under gasifying conditions thus producing a synthesis gas containing hydrogen and carbon monoxide; where the metal compound vaporizes and the vaporized metal compound reacts with the halide from the halide-containing compounds, thus producing a vaporized metal halide; cooling the vaporized metal halide, thus producing solid metal halide particles; passing the synthesis gas stream to a solids removal unit for removing the solid metal halide particles; and recovering the synthesis gas stream substantially free of halide-containing compounds.

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DESCRIPTION

METHOD OF REDUCING HALIDES IN SYNTHESIS GAS

Technical Field

The invention relates to a method for reducing halide content of a synthesis gas stream.

Background Art

The combustion of a carbonaceous material such as a solid carbonaceous fuel by reaction with a source of gaseous oxygen is well known. In such a reaction, an amount of air or oxygen equal to or greater than that required for complete combustion is used, whereby the gaseous effluent contains carbon dioxide with little, if any, carbon monoxide. It is also known to carry out the gasification or partial oxidation of solid carbonaceous materials or fuels employing a limited quantity of oxygen or air so as to produce primarily carbon monoxide and hydrogen.

Fuel sources, particularly coals, often have an undesirable halide content. The halogens in halides, such as chlorine in chlorides, form acids in the synthesis gas mixture which can cause severe corrosion in the downstream processing equipment. They also pose environmental and safety hazards if emitted to the atmosphere.

Another problem caused by the halides is reduced efficiency of the process. Formation of some salts in the synthesis gas during processing limits the overall efficiency of the heat recovery from the synthesis gas. This occurs because some salts, such as ammonium chloride, are very corrosive when permitted to condense. Thus, to avoid having the salts condense the synthesis gas cannot be cooled below the sublimation points of various salts. Since the temperature to which the synthesis gas may be cooled is thus limited, the heat recovery from the gas is accordingly limited. Chlorine-containing salts are formed due to the presence of HCl. By removing HCl from the synthesis gas, formation of such salts in the gas stream is reduced or eliminated and the gas can be cooled further to permit more thermal recovery.

A prior known method of removing HCl is by a wet absorption system. In that method the synthesis gas must be cooled and passed through an aqueous absorption column. The HCl is absorbed in the water and neutralized with NaOH. This method has drawbacks since cooling the gas to remove the HCl is inefficient and results in heat/energy loss. Additional equipment and maintenance costs also result from the addition of an absorption column to the process. Economic drawbacks also result from the need for a large water treatment plant due to build up of salts in the water from the absorption column.

It is known from U.S. Patent No. 5,118,480 to add metals such as Nahcolite to a synthesis gas downstream of the gasifier to remove HCl in conjunction with removing sulfur with a metal oxide sorbent. However, this process lacks the benefits obtained from adding the metal compound to the feed in the gasifier or before the gasifier. The salt formation reaction is believed to benefit from the dissociation and vaporization of the halide and metal compounds in the high temperatures of the gasifier.

It would be advantageous to have a practical and efficient dry method of removing the halides.

Disclosure of the Invention

The invention is a method for reducing halide content of a synthesis gas stream including:

(a) mixing a metal compound selected from the group consisting of potassium oxide, potassium hydroxide, potassium bicarbonate, potassium carbonate, sodium oxide, sodium hydroxide, sodium bicarbonate, sodium carbonate, and mixtures thereof with a carbonaceous feed material, which contains halide-containing compounds;

(b) gasifying the carbonaceous feed material in the resulting mixture in an entrained flow gasifier under gasifying conditions thereby producing a gas comprising hydrogen and carbon monoxide;

(c) where the metal compound substantially vaporizes and the vaporized metal compound reacts with the halide from the halide-containing compounds, thereby producing a vaporized metal halide;

(d) cooling the vaporized metal halide, thereby producing solid metal halide particles;

(e) removing the solid metal halide particles in the gas stream in a solids removal unit; and

(f) recovering the gas stream substantially free of halide-containing compounds.

Best Mode for Carrying Out the Invention

A. Feeds and Metal Compounds and Mixture Thereof

Several types of carbonaceous materials are suitable for feed sources. These include bituminous coal, anthracite coal, lignite, liquid hydrocarbons, petroleum coke, various organic scrap materials, municipal refuse, solid organic refuse contaminated with radioactive materials, paper industry refuse, and photographic scrap. Coal and petroleum coke are preferred feeds in this invention.

The metal compounds are those which will vaporize at the gasifier temperatures and will react with the halide present in the carbonaceous material to form a metal halide. These include potassium oxide, potassium hydroxide, potassium bicarbonate, potassium carbonate, sodium oxide, sodium hydroxide, sodium bicarbonate, and sodium carbonate. Nahcolite, a naturally occurring form of sodium bicarbonate, is preferred for its economy and availability. The metal compounds are optionally used individually or in combination.

The carbonaceous feed and the metal compounds are mixed either in the gasifier or upstream of the gasifier. A particularly efficient method of mixing is to pulverize, in the case of solid feed, both the feed and the metal compound together in the pulverizer. Either, or both, the carbonaceous feed or the metal compound are fed to the gasifier either dry or in a water slurry. If the metal compound is not mixed with the feed prior to introducing the feed into the gasifier, then it is pulverized separately from the feed and is injected independently of the feed into the gasifier. In independent injection of the metal compound, it is either transported pneumatically in nitrogen or carbon dioxide or is carried in a water slurry.

B. Reaction, Cooling, and Solids Removal

In the gasifier the carbonaceous material partially oxidizes to form synthesis gas which is primarily carbon monoxide and hydrogen. In the gasifier a substantial amount of the metal compound introduced into the gasifier is vaporized. The vaporized metal compound reacts with the halide from the halide-containing compounds from the carbonaceous materials. Metal halides are therefore formed. For example, where the metal compound is sodium bicarbonate, sodium chloride is formed. The resulting metal chloride remains in a vapor form until cooled below its sublimation point.

The synthesis gas and vaporized metal halides are then passed from the gasifier to one or more quenching and/or cooling stages. As a result of the cooling the vaporized metal halides condense to solid particles. The synthesis gas stream containing the solid metal halide particles is passed to one or more solids removal stages. The solids removal stage is preferably a cyclone or ceramic candle filter, used individually or in combination. An electrostatic precipitator is optionally used where the system pressure is at or near atmospheric. The synthesis gas recovered from the solids separation stage has reduced amounts of halides and is preferably substantially free of halides.

C. Concentrations of Halides, Ratios, and Percent Removal

The initial concentration of halides in the feed material varies widely with the type and source of the feed. Chlorine concentrations in coal range from about 0.01 %wt. to about 0.35 %wt. Other halide concentrations in coal are typically much lower than chlorine concentrations. However, even in low concentrations some halides, such as hydrogen fluoride, are very corrosive.

At least a stoichiometric amount of metal compounds must be mixed with the feed with respect to the halide concentration in the feed. Preferably, one to three times the stoichiometric ratio is used of metal compounds to halides. This assures a high degree of removal of the halides. More than about three times the stoichiometric ratio is wasteful of metal compounds and makes the process uneconomical without any apparent benefit.

From about 95 %wt. to about 99 %wt. of the halides are removed in the practice of this method. For example, the synthesis gas will contain from about 10 ppm by volume (ppmv) to about 1000 ppmv chlorine where the feed is coal. After gasification and reaction and solids removal of the metal halides, the concentration of chlorine is from about 0.1 ppmv to about 5 ppmv.

D. Operation Conditions

The gasifier is operated at gasifying conditions. These conditions may vary from feed to feed. The temperature is a temperature high enough to vaporize a substantial portion of the alkali metal compound. Vaporization of the metal compound is necessary for the metal compound to react with the halides to form metal halides. Typical temperatures in the gasifier are from about 1100°C (2000°F) to about 2000°C (3600°F). Where the feed is coal, the gasifier temperature is preferably from about 1480°C (2700°F) to about 1760°C (3200°F). The pressure of the gasifier is greater than about 300 psig and preferably from about 350 psig to about 370 psig.

CLAIMS

What is claimed is:

1. A method for reducing halide content of a gas stream comprising:

(a) admixing a metal compound selected from the group consisting of potassium oxide, potassium hydroxide, potassium bicarbonate, potassium carbonate, sodium oxide, sodium hydroxide, sodium bicarbonate, sodium carbonate, and mixtures thereof with a carbonaceous feed material, which contains halide-containing compounds;

(b) gasifying the carbonaceous feed material in the resulting mixture in an entrained flow gasifier under gasifying conditions thereby producing a gas comprising hydrogen and carbon monoxide;

(c) wherein the metal compound substantially vaporizes and the vaporized metal compound reacts with the halide from the halide-containing compounds, thereby producing a vaporized metal halide;

(d) cooling the vaporized metal halide, thereby producing solid metal halide particles;

(e) removing the solid metal halide particles in the gas stream in a solids removal unit; and

(f) recovering the gas stream substantially free of halide-containing compounds.

2. The method according to claim 1 wherein the gas comprises a synthesis gas stream derived from the gasification of coal.

3. The method according to claim 2 wherein the amount of metal compounds admixed with the feed is at least a stoichiometric amount of metal compounds with respect to the halide content of the feed.

4. The method according to claim 3 wherein the amount of metal compounds admixed with the feed is not more than about 3 times the stoichiometric amount of metal compounds with respect to the halide content of the feed.

5. The method according to claim 2 further comprising a coal pulverizing stage upstream of the gasifier and wherein the metal compound is admixed with the coal at the pulverizing stage.

6. The method according to claim 2 further comprising a coal pulverizing stage and wherein the metal compound is admixed with the coal after the pulverizing stage.

7. The method according to claim 3 wherein the metal compound is sodium bicarbonate and is dry at the point of admixture with coal.

8. A method for reducing halide content of a synthesis gas stream comprising:

(a) admixing a metal compound selected from the group consisting of potassium oxide, potassium hydroxide, potassium bicarbonate, potassium carbonate, sodium oxide, sodium hydroxide, sodium bicarbonate, sodium carbonate, and mixtures thereof with a carbonaceous feed material, which contains halide-containing compounds;

(b) feeding the resulting mixture into an entrained flow gasifier under gasifying conditions thereby producing a synthesis gas comprising hydrogen and carbon monoxide;

(c) wherein the metal compound substantially vaporizes and the vaporized metal compound reacts with the halide from the halide-containing compounds, thereby producing a vaporized metal halide;

(d) cooling the vaporized metal halide, thereby producing solid metal halide particles;

(e) passing the synthesis gas stream to a solids removal unit for removing the solid metal halide particles; and

(f) recovering the synthesis gas stream substantially free of halide-containing compounds.

9. The method according to claim 8 wherein the temperature in the gasifier is from about 1100°C to about 2000°C.

10. The method according to claim 9 wherein the temperature in the gasifier is from about 1480°C to about 1760°C.

11. The method according to claim 9 wherein the pressure in the gasifier is greater than about 300 psig.

12. The method according to claim 10 wherein the pressure in the gasifier is from about 350 psig to about 370 psig.

13. The method according to claim 8 wherein the carbonaceous material is coal, the metal compound is sodium bicarbonate, and the halide is chloride, and wherein prior to admixing the coal with the sodium bicarbonate the coal contains from about 0.01% by weight to about 0.35% by weight chlorine based on the coal as received and in the solids removal unit from about 95% by weight to about 99% by weight of the chlorine is removed in the form of sodium chloride.

14. The method according to claim 13 wherein prior to the reaction of the sodium bicarbonate with the chlorine in the gasifier the synthesis gas contains from about 10 ppmv to about 1000 ppmv chlorine based on the synthesis gas and after the solids removal unit the synthesis gas contains from about 0.1 ppmv to about 5 ppmv of the chlorine based on the synthesis gas.

15. The method of claim 8 wherein the carbonaceous feed comprises petroleum coke.

16. A method for reducing halide content of a synthesis gas stream comprising:

(a) mixing in an entrained flow gasifier under gasifying conditions a metal compound selected from the group consisting of potassium oxide, potassium hydroxide, potassium bicarbonate, potassium carbonate, sodium oxide, sodium hydroxide, sodium bicarbonate, sodium carbonate, and mixtures thereof with a carbonaceous feed material, which contains halide-containing compounds, thereby producing a synthesis gas comprising hydrogen and carbon monoxide;

(b) wherein the metal compound substantially vaporizes and the vaporized metal compound reacts with the halide from the halide-containing compounds, thereby producing a vaporized metal halide;

(c) cooling the vaporized metal halide, thereby producing solid metal halide particles;

(d) passing the synthesis gas stream to a solids removal unit for removing the solid metal halide particles; and

(e) recovering the synthesis gas stream substantially free of halide-containing compounds.

17. The method according to claim 16 wherein the temperature in the gasifier is from about 1100°C to about 2000°C and wherein the pressure in the gasifier is greater than about 300 psig.

18. The method according to claim 17 wherein the metal compound is sodium bicarbonate and is dry at the point of admixture with coal.

INTERNATIONAL SEARCH REPORT

Inter. .onal Application No
PCT/US 94/03820

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C10J3/46

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)
IPC 5 C10J C10K

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 practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE,A,41 09 231 (DEUTSCHES BRENNSTOFFINSTITUT) 24 September 1992 see column 4, line 54 - column 5, line 7 see column 7-8; claims 1-7 ---	1,2,8,9, 11,13
A	DE,A,33 32 913 (CHEM. FABR. UETIKON) 13 December 1984 see page 1-3; claims 1-14 ---	1-3
A	US,A,4 277 365 (PAULL) 7 July 1981 see column 3, line 33-40 see column 5-6; claims 1-8 ---	1,2,8-12
A	US,A,4 436 531 (ESTABROOK) 13 March 1984 see column 3, line 16-29 see column 9, line 16-34 ---	1,2, 8-12, 15-17
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,A	NL,A,9 101 793 (HOOGOVENS GROEP) 17 May 1993 -----	

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte onal Application No
PCT/US 94/03820

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US-A-4277365	07-07-81	NONE		
US-A-4436531	13-03-84	NONE		
NL-A-9101793	17-05-93	NONE		