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

(57) Abstract

The invention is a method for reducing the hydrogen cyanide content of a synthesis gas stream including mixing an iron compound with a nitrogen- containing coal feed; gasifying the coal feed in the resulting mixture in an entrained flow gasifier under gasifying conditions thereby producing a gas comprising hydrogen and carbon monoxide and where at least a portion of the nitrogen forms hydrogen cyanide; where the iron compound catalytically converts at least a portion of the nitrogen in the hydrogen cyanide to gaseous molecular nitrogen; and recovering the gas stream having substantially reduced amounts of hydrogen cyanide.

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DESCRIPTION

METHOD OF REDUCING HCN IN SYNTHESIS GAS

Technical Field

The invention relates to a method for reducing the hydrogen cyanide 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.

Various problems are associated with the different types of feeds utilized in gasification processes. With liquid hydrocarbon and petroleum coke feeds there is insufficient ash content in the feed to create a slag having an adequate viscosity. The slag is formed from the incombustible mineral content of the feed and forms an insulating layer on the gasifier walls which protects the walls from the high temperatures of the reaction. Nickel and vanadium content is also a problem in such feeds. Optimum slag viscosity is necessary to adsorb and remove nickel and vanadium metals, thus reducing their presence in the synthesis gas and the reactor. It is taught in U.S. Patent No. 4,668,428 that adding iron additives to liquid hydrocarbon and petroleum coke feeds to a gasifier can be beneficial in reducing the viscosity of the slag. This results in washing the vanadium and nickel captured in the slag out of the gasifier.

The problem of insufficient ash is not present in coal since coal has from 10-20 percent by weight ash and petroleum coke and heavy liquid hydrocarbons only have from one-half to 5 percent by weight. Coal feeds, however, present different problems. Coal typically has an undesirable nitrogen content, i.e., "coal nitrogen." The nitrogen in the coal, upon gasification of the coal, forms hydrogen cyanide and ammonia in the synthesis gas mixture. These compounds cause severe corrosion in the downstream processing equipment. The compounds also pose environmental and safety hazards if emitted into the atmosphere. It would be advantageous to have a practical and efficient method of removing the hydrogen cyanide and ammonia from the synthesis gas.

Disclosure of the Invention

The invention is a method for reducing the hydrogen cyanide content of a synthesis gas stream including:

(a) mixing an iron compound with a nitrogen containing coal feed;

(b) gasifying the coal feed in the resulting mixture in an entrained flow gasifier under gasifying conditions thereby producing a gas comprising hydrogen and carbon monoxide and wherein at least a portion of said nitrogen forms hydrogen cyanide;

(c) wherein the iron compound catalytically converts at least a portion of the nitrogen in said hydrogen cyanide to gaseous molecular nitrogen; and

(d) recovering the gas stream having substantially reduced amounts of hydrogen cyanide.

Best Mode for Carrying Out the Invention

A. Feeds and Iron Compounds and Mixture Thereof

Several types of coals are suitable for feed sources. These include bituminous coal, anthracite coal, and lignite. The iron compounds for use with the process of this invention are those which will catalytically convert the nitrogen in hydrogen cyanide and ammonia to gaseous molecular nitrogen. These compounds include iron oxides, such as ferric oxide and ferrous oxide. The term "iron compounds" as used in this specification and the appended claims includes elemental iron. Elemental iron is available, for example, from machine shop waste. Ferric oxide is preferred for its economy and availability. The iron compounds are optionally used individually or in combination.

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

B. Reaction, Conversion, Cooling, and Solids Removal

In the gasifier the coal partially oxidizes to form synthesis gas which is primarily carbon monoxide and hydrogen. In the gasifier a substantial amount of the iron compound interacts with the evolving gases, particularly HCN. The iron compound catalytically converts the nitrogen in the hydrogen cyanide and/or ammonia to gaseous molecular nitrogen.

The synthesis gas and gaseous molecular nitrogen are then passed from the gasifier to one or more quenching and/or cooling stages. Flyash is cooled to condense to solid particles. The synthesis gas stream containing the solid 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 is at or near atmospheric pressure. The synthesis gas recovered from the solids separation stage has reduced amounts of hydrogen cyanide and/or ammonia.

C. Concentrations of Iron Compound and Percent Removal

The concentration of iron compounds in the feed material varies widely with the type and source of the feed. As a result, varying levels of iron compound are needed to correspond to the nitrogen level in the feed and the desired level of hydrogen cyanide and/or ammonia reduction.

At least an effective amount of iron compound is added to catalytically convert a portion of the nitrogen in the hydrogen cyanide and/or ammonia to gaseous molecular nitrogen. The amount of iron added is not more than about 5 percent by weight based on the weight of the coal feed. Preferably, the amount or iron mixed with the feed is from about 2 percent iron by weight to about 3 percent iron by weight based on the coal feed. This assures a high degree of conversion of the nitrogen. More than about 5 percent is wasteful of the iron compounds and makes the process uneconomical without any apparent benefit.

In typical coal gasification operations without catalytic aid, about 90 percent by weight of the coal nitrogen is converted to gaseous molecular nitrogen and the remaining 10 percent by weight is converted to HCN or ammonia. With the addition of the iron catalyst from about 35 percent by volume to about 95 percent by volume of the nitrogen in both the hydrogen cyanide and/or ammonia is converted to gaseous molecular nitrogen. More preferably, at least about 90 percent by volume of the combined total of the nitrogen in the hydrogen cyanide and/or ammonia is converted to gaseous molecular nitrogen. Thus, by addition of the iron compound the overall conversion of coal nitrogen to gaseous molecular nitrogen is increased to from about 95 percent to about 99 percent by weight of the coal nitrogen in the feed.

Prior to catalytic conversion, the synthesis gas contains a combined total of from about 500 ppmv to about 800 ppmv hydrogen cyanide and/or ammonia based on the synthesis gas. After the conversion of the nitrogen in the hydrogen cyanide and/or ammonia to gaseous molecular nitrogen the synthesis gas contains a combined total of from about 50 ppmv to about 360 ppmv of hydrogen cyanide and ammonia based on the synthesis gas. Preferably, the combined total is not more than about 50 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 gasify a substantial portion of the coal feed. Typical temperatures in the gasifier are from about 1100°C (2000°F) to about 2000°C (3600°F). 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.

Illustrative Embodiment

The following illustrated embodiment is not intended to limit the scope of the invention.

In this embodiment a 250 ton/day dry feed entrained flow coal gasification reactor was operated with a feed of various coals as identified in the Table below. The temperature in the contacting zone was between 1480°C and 1760°C and the pressure was between 350 psig and 370 psig. The iron compound was iron-rich flyash from previous gasification runs. It was added to the coal feed before the pulverizer so that the coal was mixed with the iron compound in the pulverizer. The results in the Table below show the effect of adding varying amounts of an iron compound to the coal feed. The Table shows the effect of iron on reducing concentrations of hydrogen cyanide and ammonia in synthesis gas.

TABLE

REDUCTION OF HCN AND NH_3 BY ADDITION OF IRON TO FEED

COAL FEED	CONCENTRATION OF IRON (%wt.)	CONCENTRATION OF HCN (PPMV)	CONCENTRATION OF NH_3 (PPMV)	CONCENTRATION OF HCN AND NH_3 (PPMV)
Drayton	0.82	156	62	218
Drayton	1.24	108	63	171
Illinois, #5	1.41	61	35	96
Illinois, #5	2.05	15	30	45
Pike County	0.29	240	260	500
Pike County	0.84	180	140	320

CLAIMS

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

(a) admixing an iron compound with a nitrogen-containing coal feed;

(b) gasifying the coal feed in the resulting mixture in an entrained flow gasifier under gasifying conditions thereby producing a gas comprising hydrogen and carbon monoxide and wherein at least a portion of said nitrogen forms hydrogen cyanide;

(c) wherein the iron compound catalytically converts at least a portion of the nitrogen in said hydrogen cyanide to gaseous molecular nitrogen; and

(d) recovering the gas stream having substantially reduced amounts of hydrogen cyanide.

2. The method according to claim 1 wherein the temperature in the gasifier is from about 1480°C to about 1760°C.

3. The method according to claim 2 wherein the amount of iron compound admixed with the feed is not more than about 5 percent iron by weight based on the coal feed.

4. The method according to claim 2 wherein the amount of iron compound admixed with the feed is from about 2 percent iron by weight to about 3 percent iron by weight based on the coal feed.

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

7. The method according to claim 3 wherein the iron compound is ferrous oxide or ferric oxide.

8. The method according to claim 3 wherein the iron compound is elemental iron.

9. A method for reducing the hydrogen cyanide and ammonia content of a gas stream comprising:

(a) admixing an iron compound with a nitrogen-containing coal feed;

(b) gasifying the coal feed in the resulting mixture in an entrained flow gasifier under gasifying conditions thereby producing a gas comprising hydrogen and carbon monoxide and wherein at least a portion of said nitrogen forms hydrogen cyanide and ammonia;

(c) wherein the iron compound catalytically converts at least a portion of the nitrogen in said hydrogen cyanide and ammonia to gaseous molecular nitrogen; and

(d) recovering the gas stream having substantially reduced amounts of hydrogen cyanide and ammonia.

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

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

12. The method according to claim 10 wherein the pressure in the gasifier is greater than about 300 psig.

13. The method according to claim 11 wherein the pressure in the gasifier is from about 350 psig to about 370 psig.

14. The method according to claim 9 wherein the iron compound is ferric oxide and wherein from about 35 percent by volume to about 95 percent by volume of the nitrogen in both the hydrogen cyanide and ammonia is converted to gaseous molecular nitrogen.

15. The method according to claim 9 wherein the iron compound is ferric oxide and wherein at least about 90 percent by volume of the combined total of the nitrogen in

the hydrogen cyanide and ammonia is converted to gaseous molecular nitrogen.

16. The method according to claim 14 wherein prior to the conversion of the nitrogen in the hydrogen cyanide and ammonia to gaseous molecular nitrogen, the synthesis gas contains a combined total of from about 500 ppmv to about 800 ppmv hydrogen cyanide and ammonia based on the synthesis gas and after the conversion of the nitrogen in the hydrogen cyanide and ammonia to gaseous molecular nitrogen the synthesis gas contains a combined total of from about 50 ppmv to about 360 ppmv of hydrogen cyanide and ammonia based on the synthesis gas.

17. A method for reducing the hydrogen cyanide content of a gas stream comprising:

(a) admixing in a coal pulverizing stage a ferric oxide with a nitrogen containing coal feed wherein the amount of iron admixed is from about 2 percent iron by weight to about 3 percent iron by weight based on the coal feed;

(b) gasifying the coal feed in the resulting mixture in a dry-feed entrained flow gasifier, wherein the pressure in the gasifier is greater than about 300 psig and wherein the temperature in the gasifier is from about 1480°C to about 1760°C, thereby producing a gas comprising hydrogen and carbon monoxide and wherein at least a portion of said nitrogen forms hydrogen cyanide;

(c) wherein the ferric oxide catalytically converts at least about 90 percent by volume of the nitrogen in the hydrogen cyanide to gaseous molecular nitrogen; and

(d) recovering the gas stream having less than about 50 ppmv of hydrogen cyanide.

18. The method according to claim 17 wherein the ferric oxide is dry at the point of admixture with said coal.

INTERNATIONAL SEARCH REPORT

Inte[...]onal Application No
PCT/US 94/04794

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C10J3/46 C10J3/00

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

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	US,A,4 437 417 (ROBERTS) 20 March 1984 see column 9-10; example 1 see column 10-11; claim 1 see column 12; claims 14,15 ---	1-4
A	US,A,4 170 550 (KAMODY) 9 October 1979 see column 9, line 26 - column 11, line 45 see column 12, line 38 - column 15, line 15 ---	1,2,5, 9-13
A	US,A,2 691 573 (MAYLAND) 12 October 1954 see column 2, line 11 - column 3, line 46 ---	1,5,6
A	EP,A,0 150 164 (BERG) 31 July 1985 see page 9; claims 1-3 -----	1,5-7

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

☒ Patent family members are listed in annex.

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Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

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