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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) Inventors: CLOMBURG, Lloyd, Anthony, Jr.; 18207 Widcombe Drive, Houston, TX 77084 (US). PARUCHURI, Eswarachandra, Kumar; 8814 Chelsworth, Houston, TX 77083 (US). 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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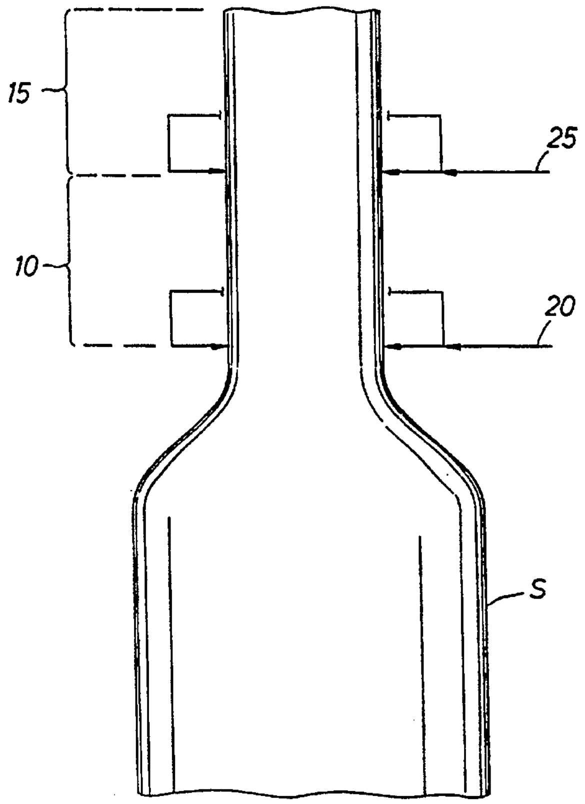
(54) Title: METHOD OF QUENCHING SYNTHESIS GAS

(57) Abstract

The invention is a process for quenching a first synthesis gas mixture containing synthesis gas, molten flyash, water, and carbon dioxide and producing additional synthesis gas consisting of (a) passing the first synthesis gas mixture into a first quench zone; (b) introducing into the quench zone a mixture of pulverized coal in a nitrogen or carbon dioxide carrier gas; (c) endothermically reacting the pulverized coal with the water and the carbon dioxide in the synthesis gas mixture thus producing additional synthesis gas consisting of hydrogen and carbon dioxide and wherein the additional synthesis gas is admixed with the first synthesis gas mixture to form a second synthesis gas mixture; (d) passing the second synthesis gas mixture to a second quench zone; (e) introducing into the second quench zone a cooling gas for admixture with the second synthesis gas mixture, thus cooling the second synthesis gas mixture, where the molten flyash is solidified, and thus forms a third synthesis gas mixture; and (f) passing the third synthesis gas mixture to a solids removal stage for removing the solidified flyash.



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DESCRIPTION

METHOD OF QUENCHING SYNTHESIS GAS

Technical Field

The invention relates to a two-stage quenching method for a synthesis gas stream by first injecting coal particulates into the gasifier effluent and then injecting a cooling gas into the resulting mixture.

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 known also 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.

The gases resulting from partial combustion or gasification of solid carbon-containing fuels such as coal have value as residential and industrial fuels. They also have value as starting materials for synthesis of chemicals and fuels and as an energy source for generation of electricity. These uses have long been recognized and partial gasification has been practiced on varying scales throughout the world. In the case of coal gasification, a number of different gasification processes have been developed to take into account factors such as the coal source employed, the gasifying medium used and the use sought to be made of the product gas.

While these processes may be classified in a variety of ways, they generally fall into two distinct groups. The two groups are distinguished with respect to the condition in which the non-carbonaceous, mineral residue is removed from the gasification zone. The residue is removed as a dry ash in a nonslagging operation or as a slag in a slagging operation. These two processes are different primarily due to the temperatures employed in the gasification zone itself. The nonslagging gasifiers are operated at lower reaction temperatures, usually less than 1400°C. This is below the temperature at which the contained ash will fuse. The temperatures employed in slagging gasifiers are usually 1500-2700°C. These temperature are sufficient to convert the dry ash into a molten slag.

Advantages exist for gasification processes in each of the two process groups. The processes employing slagging coal gasifiers, however, are generally considered to be the most flexible at least in terms of the variety of coal feedstocks which can be employed. The operation of coal gasifiers under nonslagging conditions is generally limited to coals of low ash content because of the difficulty in removing ash with grates and other mechanical devices. In contrast, in operation at slagging conditions almost any coal can be suitably employed because the ash becomes a free-flowing fluid under slagging conditions. As a result, the fluid ash is quite simply and easily removed from the gasifier. A good general review of a variety of coal gasification processes appears in the Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Ed., Vol. 10, pp. 353-388, Interscience (1966).

One process employing a slagging coal gasifier which has had rather wide application is the Koppers-Totzek process. This process which is described in an article by F. Totzek in "Brennstoff-Chemie," Vol. 34, pp. 361-367 (1953), has the capability of handling just about any coal including lignites with up to 30% ash or mineral contents. A significant portion of the molten slag is removed at the bottom of the gasifier. However, the product gas of this process, like other processes employing slagging gasifiers, still contains a significant quantity of mineral matter. The mineral matter is in the form of a suspension or mist of molten or partly molten particles. In this molten state the ash is sticky.

The slag in coals is caused primarily because of the impure nature of coal and the mineral matter in typical coals. These impurities include mixtures of silica and various metal oxides. The molten or partly molten slag will not have a specific melting point. Instead it will solidify over a wide melting range which may cover many hundreds of degrees which can make processing difficult.

It is typically desired to cool the coal gasifier effluent prior to further processing. In a typical application, the gas leaving the reactor has a temperature, as a rule, higher than 1400°C (2552°F), preferably from about 2650°F to about 3000°F, at which the ash is quite fluid. For further processing, this crude product gas is typically cooled down to, for example 300°C (572°F). In the cooling the gas will pass through a broad range of temperatures at which the slag is sticky. The slag from coal usually is sticky at temperatures greater than about 1700°F (927°C). Once the slag particles are no longer sticky, they can be easily removed by known techniques such as cyclones, bind separators, filters or similar devices.

In the transition between being highly fluid molten liquid and solid nonsticky particles, these slag particles exhibit sufficient stickiness that they can cause extreme difficulties in processing. That is, the slag adheres to and forms deposits on walls, valves, outlets, etc., of process equipment immediately downstream of the gasifier. These deposits tend to build up and as a result interfere with good operation of the process and even lead to complete blocking.

A previous process has added coal directly to the cooling gas (see U.S. Patent No. 4,054,424). Such a process is disadvantageous, however, since the gas mixture is cooled too much to provide complete reaction of the added coal particles. As a result, undesirable hydrocarbons may be formed, such as ringed compounds, that will have to be removed thus requiring additional processing.

Another previous process, disclosed in U.S. Patent No. 2,987,387, provides for diverting of vaporized slurry feed water (i.e., steam) in excess of that required for gasification temperature control. The excess is diverted for use in quenching the gasifier effluent. The diverted excess contains only trace amounts of reactive materials such as powdered or volatilized coal. The weight ratio of steam to coal is less than 1 to 0.1. The excess steam reacts with unreacted coal in the gasifier effluent as well as the trace coal in the excess steam. The addition of steam can cause plugging and fouling problems since it is a condensible substance. In a dry feed system, the addition of steam can wet the coal particles, forming a "mud." Any condensed steam will also have to be separated. Thus another separations unit is required.

Accordingly, it would be advantageous to have a process for cooling the product gas of a slagging coal gasifier in which the harmful effects of the stickiness of molten slag particles contained therein is minimized or even completely eliminated and the disadvantages of previously known processes are avoided.

Disclosure of the Invention

The invention is a process for quenching a first synthesis gas mixture containing synthesis gas, molten flyash, water vapor, and carbon dioxide and producing additional synthesis gas by a process including the following steps:

a. passing the first synthesis gas mixture into a first quench zone;

b. introducing into the quench zone a mixture of a major amount of pulverized coal and a minor amount of carrier gas;

c. endothermically reacting the pulverized coal with the water vapor and the carbon dioxide in the synthesis gas mixture thus producing additional synthesis gas consisting of hydrogen and carbon monoxide and wherein the additional synthesis gas is admixed with the first synthesis gas thereby forming a second synthesis gas mixture;

d. passing the second synthesis gas mixture to a second quench zone;

e. introducing into the second quench zone a cooling gas for admixture with the second synthesis gas mixture, thereby cooling the second synthesis gas mixture and solidifying the molten flyash, thereby forming a third synthesis gas mixture; and

f. passing the third synthesis gas mixture to a solids removal stage for removing the solidified flyash.

This invention provides an improved method for cooling the hot synthesis gas obtained when coal is partially oxidized in an entrained flow slagging coal gasifier. More particularly, this invention provides a process for direct two-stage quenching of the hot synthesis gas of a slagging coal gasifier in two quench zones. The benefit of this process is achieving enhanced efficiency in recovering the energy value of the coal while at the same time minimizing or avoiding the deposition of sticky, molten slag particles on the quench zone walls. It is important to prevent such deposition of sticky slag particles on the process equipment downstream of the gasifier since such deposition can foul and block the equipment.

Best Mode for Carrying Out the Invention

A. Feeds and Feed Preparation

The coal feedstocks employed in the invention generally encompass any coal available in commercial quantities including anthracite, bituminous, sub-bituminous and lignite having mineral contents ranging from less than 5% by weight up to 30% by weight or more. The coal feed is pulverized in a pulverizer. The coal is optionally fed to the gasifier dry or in a water slurry. Dry feed is transported pneumatically in nitrogen or carbon dioxide.

B. Gasifier Types

The process of the invention is applicable to the quenching of the gas effluent of any conventional slagging coal gasifier whether it be fixed or fluidized bed, fully entrained suspension or otherwise operated under atmospheric or superatmospheric conditions with the only proviso being that the synthesis gas mixture contain some mineral matter in the form of molten or partly molten particles.

In general, these slagging coal gasifiers are operated under partial oxidation conditions to yield CO, H_2 and CO_2 as the principal gaseous products with methane, water vapor and nitrogen also being present in certain cases. The latter two components are prevalent when steam, air or oxygen-enriched air are employed in the gasifying medium. When operated under slag-forming conditions, the product gas, i.e., first synthesis gas mixture, emanating from the gasifier will generally be at a temperature higher than 1400°C. It contains a suspension or fine mist of sticky molten or partly molten mineral slag particles.

C. Gasifier Operating Conditions

The gasifier is operated at gasifying conditions. These conditions may vary from feed to feed. 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.

D. First Quench Zone

The synthesis gas, water vapor, carbon dioxide, and molten slag, i.e., first synthesis gas mixture, are then passed from the gasifier to two or more quenching and/or cooling stages. According to the invention, this first synthesis gas mixture is cooled in a first quench zone. This is achieved by direct mixing of the first synthesis gas with a major amount of pulverized coal in a minor amount of a gas carrier. As used herein and in the pending claims, "major amount" means greater than 50 percent by weight and "minor amount" means less than 50 percent by weight. Preferably, the weight ratio of coal to carrier gas is greater than 10 to 1. The carrier gas may be any gas that can be mixed with the first synthesis gas mixture without adversely effecting its quality for the desired use. The two gases need not be the same. The carrier gas is preferably a gas such as nitrogen or carbon dioxide which is noncondensible under the operating conditions of the process. The carbon in the injected coal will react with carbon dioxide and water in the first synthesis gas mixture to form additional synthesis gas containing carbon monoxide and hydrogen. The reaction equations are as follows:

$$C + H_2O = CO + H_2$$
$$C + CO_2 = 2\ CO$$

This mixing of additional synthesis gas with the first synthesis gas mixture results in a second synthesis gas mixture which is further cooled in the second quench zone. The first synthesis gas mixture of gasification enters the first quench zone at conventional flow rates of, e.g., greater than about 10 kg/sec, preferably about 20 kg/sec to about 100 kg/sec. The pulverized coal in a carrier gas is most suitably introduced at the entrance of the first quench zone.

About 0.5 to about 2 times the stoichiometric amount of coal for the production of hydrogen and carbon monoxide from the water vapor and carbon dioxide in the first synthesis gas mixture are mixed with the first synthesis gas mixture. Since the above reactions are endothermic processes the first synthesis gas mixture is cooled by the heat adsorbed in the reaction. The cooling is not below the temperature at which the added coal is completely reacted so that undesirable hydrocarbons are not formed. This second synthesis gas mixture leaves the first quench zone and enters the second quench zone at a temperature from about 1900°F to about 2400°F, preferably from about 2100°F to about 2400°F.

E. <u>Second Quench Zone</u>

In a second quench zone, the gas from the first quench zone is further cooled by contact with a gas at a lower temperature. The cooling of a gas by intimate mixing with a gas at a lower temperature is very effective and involves no delay. Cooling is thus rapidly effected in a relatively small space. This has great advantages, because the temperature range in which the slag particles are sticky is passed through rapidly, so that the second synthesis gas mixture cooling zone can be small, but sufficient to cool the slag to solidification.

The quantity of cooling gas required naturally depends on the desired degree of cooling, on the nature and the temperature of the cooling gas, the temperature of the second synthesis gas mixture and the nature of the slag particles. The cooling is to a sufficient degree to solidify the slag particles. The cooling medium is water vapor or any gas that can be mixed with the second synthesis gas mixture without adversely effecting its quality for the desired use. These gases include nitrogen, recycled cooled synthesis gas, water, or steam.

The mixing of the second synthesis gas mixture with the cooling gas results in a third synthesis gas mixture. The cooling of the second synthesis gas mixture progresses to the temperature where the slag particles are no longer sticky. This mixture includes the entrained slag. The slag has been condensed to solid particles. These particles are then easily removed. The third synthesis gas mixture leaves the second quench zone at a temperature from about 1500°F to about 1900°F, preferably from about 1600°F to about 1700°F. The cooling gas is introduced downstream of the first quench zone. This cooling gas is optionally introduced through radially directed outlets located at about the same height and equally spaced around the circumference of the quench zone.

F. <u>Quench Zone Physical Parameters</u>

The coal and carrier gas and cooling gas, in the first and second quench zones, respectively, are introduced into the first synthesis gas mixture and second synthesis gas mixture, respectively, in the form of gas jets. In addition, cooling gas outlets are not located in the stream of synthesis gas mixtures containing sticky slag particles, so that fouling of the outlets is prevented. In most applications the volume ratio of second synthesis gas mixture to cooling gas is suitably from 1:0.5 to 1:3.0 with ratios of about 1:0.5 being preferred.

The quench zone is preferably tubular. The diameter of the radially directed cooling gas outlets is chosen such that the gas jets are sufficiently strong to reach the center of the quench zone. Stable gas jets are obtained at a linear gas velocity of about 5 m/s to about 30 m/s.

The distance between the cooling gas inlets in the second quench zone and the coal and carrier gas inlets of the first quench zone will depend on several variables including velocity of the gas stream, diameter of the quench zone, desired conversion of coal, desired cooling, and economic considerations since a longer pressurized zone is more expensive. This distance can be determined by one of ordinary skill in the art once the desired variables are selected.

The first quench zone used in the process according to the invention includes a tube that can be connected to a source of the first synthesis gas mixture to be cooled. The tube is provided with an gas inlet located in the vicinity of that connection. The tube has two or more inlets for providing gas in an annular, radial, or tangential direction. The inlets are equally spaced around the circumference of the quench zone.

G. Solids Removal Stage

As a result of the cooling the molten slag will condense to form solid particles. The synthesis gas stream containing the solid particles is then passed to one or more solids removal stages. The solids removal stages are 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 solids and is preferably substantially free of solids.

H. Detailed Description of the Figure

The invention will now be further described with the aid of the sole Figure which is a schematic representation of a two-stage quench zone according to the invention.

The Figure depicts a top portion of a slagging coal gasification reactor 5 connected to a first tubular quench zone 10 and a second tubular quench zone 15. Coal particles are partially oxidized in the reactor 5 to produce a first synthesis gas. The gas so produced has a temperature of 1600°C and consists mainly of CO and H_2 but further contains CO_2, H_2O and possibly N_2, as well as the finely dispersed molten slag particles. These particles are liquid at 1600°C. The first synthesis gas mixture passes from the reactor 5 to the first quench zone 10.

As seen in the Figure, powdered coal and carrier gas are introduced through the pulverized coal introduction inlets 20 formed in the wall of the first tubular quench zone near the joint between the reactor 5 and the first quench zone 10. The pulverized coal inlets 20 supply the pulverized coal and carrier gas mixture to the first quench zone. There are several pulverized coal introduction ducts 20 at different angles relevant to the quench zone center axis.

The pulverized coal is endothermically reacted with components of the first synthesis gas mixture. Additional synthesis gas is produced and mixes with the first synthesis gas mixture, resulting in a second synthesis gas mixture. This second synthesis gas mixture passes out of the first quench zone 10 into second tubular quench zone 15. Through ports 25 in the wall of the second quench zone 15, a cooling gas is supplied. This cooling gas penetrates into the second synthesis gas mixture in the form of jets of gas. Ports 25 may have different diameters and are equally spaced around the circumference wall.

The second synthesis gas mixture is cooled by this cooling gas to a temperature from about 1500°F to about 1900°F, at which the slag particles have lost their stickiness. The solid particles are then removed by a cyclone or ceramic candle filter (not shown).

CLAIMS

1. A process for quenching a first synthesis gas mixture comprising synthesis gas, molten flyash, water, and carbon dioxide and producing additional synthesis gas comprising:

a. passing said first synthesis gas mixture into a first quench zone;

b. introducing into said quench zone a mixture of a major amount of pulverized coal and a minor amount of carrier gas;

c. endothermically reacting said pulverized coal with said water and the carbon dioxide in said synthesis gas mixture thereby producing additional synthesis gas comprising hydrogen and carbon monoxide and wherein said additional synthesis gas is admixed with said first synthesis gas mixture thereby forming a second synthesis gas mixture;

d. passing said second synthesis gas mixture to a second quench zone;

e. introducing into said second quench zone a cooling gas for admixture with said second synthesis gas mixture, thereby cooling said second synthesis gas mixture, solidifying said molten flyash, and thereby forming a third synthesis gas mixture; and

f. passing said third synthesis gas mixture to a solids removal stage for removing the solidified flyash.

2. The process according to claim 1 wherein the weight ratio of coal to carrier gas in said mixture in step (b) is at least 10 to 1.

3. The process according to claim 1, wherein the cooling gas is nitrogen, recycled cooled synthesis gas, water, or steam.

4. The process according to claim 1, wherein the second quench zone is immediately downstream of the first quench zone.

5. The process according to claim 4, wherein the volume ratio between the flow of the second synthesis gas mixture and cooling gas ranges from about 1:0.1 to about 1:1.5.

6. The process according to claim 5, wherein the volume ratio between the flow of the second synthesis gas mixture and cooling gas is about 1:0.5.

7. The process according to claim 4, wherein the carrier gas is nitrogen or carbon dioxide.

8. The process according to claim 7, wherein said outlets are at different angles relevant to the quench zone center axis.

9. The process according to claim 8, wherein a portion of the outlets inject radially into the quench zone.

10. The process according to claim 5, wherein the cooling gas is injected at a linear velocity ranging from about 5 m/sec to about 30 m/sec.

11. The process according to claim 4 wherein the amount of pulverized coal admixed with the first synthesis gas mixture is from about 0.5 to about 2 times the stoichiometric amount of coal for the production of hydrogen and carbon monoxide from the water and carbon dioxide in the first synthesis gas mixture.

12. The process according to claim 11 wherein the solids removal unit is a cyclone or filter.

13. The process according to claim 12 wherein the filter is a ceramic candle filter.

14. The process according to claim 3 wherein the temperature of the first synthesis gas mixture entering the first quench zone is from about 2650°F to about 3000°F.

15. The method according to claim 14 wherein the temperature of the second synthesis gas mixture entering the second quench zone is from about 1900°F to about 2400°F.

16. The method according to claim 15 wherein the temperature of the third synthesis gas mixture passing out of the second quench zone is from about 1500°F to about 1900°F.

17. The method according to claim 3 wherein the pressure of the first synthesis gas mixture entering the first quench zone greater than about 300 psig.

18. The method according to claim 17 wherein the pressure of the first synthesis gas mixture entering the first quench zone from about 350 psig to about 370 psig.

19. A process for quenching a first synthesis gas mixture comprising synthesis gas, molten flyash, water, and carbon dioxide and producing additional synthesis gas comprising:

a. passing said first synthesis gas mixture into a first quench zone;

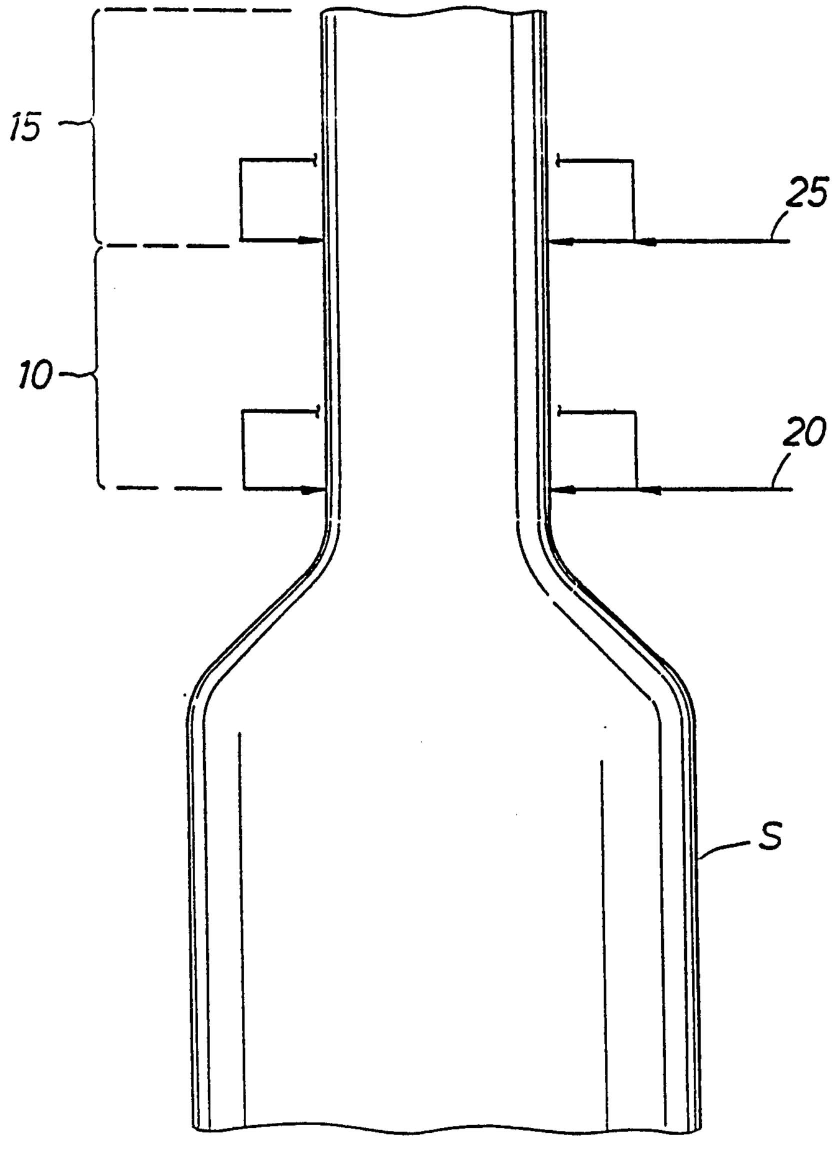
b. introducing into said quench zone a mixture of pulverized coal and nitrogen, wherein the weight ratio of coal to nitrogen is at least 10 to 1;

c. endothermically reacting said pulverized coal with said water and the carbon dioxide in said synthesis gas mixture thereby producing additional synthesis gas comprising hydrogen and carbon monoxide and wherein said additional synthesis gas is admixed with said first synthesis gas mixture thereby forming a second synthesis gas mixture having a temperature from about 1900°F to about 2400°F;

d. passing said second synthesis gas mixture to a second quench zone;

e. introducing into said second quench zone a cooling gas for admixture with said second synthesis gas mixture, thereby cooling said second synthesis gas mixture to a temperature from about 1600°F to about 1700°F, solidifying said molten flyash, and thereby forming a third synthesis gas mixture; and

f. passing said third synthesis gas mixture to a cyclone for removing the solidified flyash.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INTERNATIONAL SEARCH REPORT

Inte nal Application No
PCT/US 94/05405

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C10J3/84 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

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	EP,A,0 423 401 (THE DOW CHEMICAL CO.) 24 April 1991 see page 3, column 4, line 19 - page 5, column 7, line 48 see page 7-8; example 6 ---	1,3,12, 14,15, 17-19
A	GB,A,2 051 121 (AVCO EVERETT RES. LAB.) 14 January 1981 see page 4, line 74 - page 5, line 46 ---	1-4,14, 17,19
A	FR,A,2 401 982 (COMBUSTION ENGINEERING) 30 March 1979 see page 3, line 2 - page 4, line 36 ---	1,14,15, 19
A	FR,A,2 261 974 (SHELL) 19 September 1975 see page 1, line 13 - page 4, line 29 --- -/--	1,7,14, 15,18,19

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

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search 30 August 1994	Date of mailing of the international search report -5. 09. 94
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INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/US 94/05405

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	FR,A,2 177 089 (BITUMINOUS COAL RES.) 2 November 1973 -----	

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 94/05405

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0423401	24-04-91	US-A-	4872886	10-10-89
		CA-A-	2000446	11-04-91
		WO-A-	9105835	02-05-91
		AU-B-	593860	22-02-90
		AU-A-	6572186	04-06-87
		DE-A-	3685559	09-07-92
		EP-A,B	0225146	10-06-87
		JP-A-	62131094	13-06-87
GB-A-2051121	14-01-81	US-A-	4278445	14-07-81
		DE-A,C	3020684	11-12-80
		FR-A,B	2457889	26-12-80
		JP-A-	55161888	16-12-80
FR-A-2401982	30-03-79	US-A-	4158552	19-06-79
		AU-B-	514817	26-02-81
		AU-A-	3764878	03-01-80
		CA-A-	1092822	06-01-81
		DE-A,C	2831027	22-03-79
		JP-C-	1304436	28-02-86
		JP-A-	54046201	12-04-79
		JP-B-	60030356	16-07-85
		SE-A-	7809013	01-03-79
FR-A-2261974	19-09-75	GB-A-	1491465	09-11-77
		AU-A-	7833875	19-08-76
		CA-A-	1050271	13-03-79
		DE-A-	2507124	28-08-75
		JP-C-	1217052	17-07-84
		JP-A-	50119006	18-09-75
		JP-B-	58051036	14-11-83
		NL-A-	7501943	25-08-75
		US-A-	4060397	29-11-77
FR-A-2177089	02-11-73	CA-A-	991853	29-06-76
		DE-A-	2312283	11-10-73
		GB-A-	1393636	07-05-75
		JP-C-	875698	10-08-77
		JP-A-	49007306	23-01-74
		JP-B-	52002924	25-01-77

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte ɔnal Application No

PCT/US 94/05405

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR-A-2177089		US-A- 3782913	01-01-74

Form PCT/ISA/210 (patent family annex) (July 1992)