EUROPEAN PATENT SPECIFICATION

PARTIAL OXIDATION PROCESS WITH SOOT FILTER CAKE RECOVERY

TEIOXIDATIONSVERFAHREN MIT RÜCKGEWINNUNG VON RUSSFILTERMASSEN

PROCEDE D'OXYDATION PARTIELLE AVEC RECUPÉRATION DU GATEAU DE FILTRATION DE SUIE

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Description

FIELD OF THE INVENTION

[0001] This invention is directed to improvements in the process of partial oxidation of hydrocarbonaceous feedstocks to produce synthesis gas or syngas mixtures comprising H₂, CO, and other gaseous materials. In particular, the improvements relate to the recovery of unreacted carbon and to temperature moderation of the gasification reactor used to produce the syngas, wherein a hydrocarbonaceous feed in admixture with a dispersion of recycled carbon-soot is introduced into a gasification system, particularly an oil-fed gasification system.

BACKGROUND OF THE INVENTION

[0002] The production of syngas from hydrocarbonaceous feedstocks requires the addition of oxygen to the syngas reactor, which is also known as a syngas generator, or gasifier. Such processes also require the addition of a moderator such as CO₂, steam or water to maintain the reactor temperature within permissible limits set by the economics of the operation and the limits of the reactor’s refractory materials of construction.

[0003] A problem associated with the partial oxidation gasification process is the presence of unreacted or unconverted carbon, mostly in the form of soot, in the raw syngas product. Several techniques can be used to remove the soot, the most common being to scrub the syngas product with water in a scrubber where the entrained carbon is transferred to the scrubbing water and a scrubbed soot-free syngas is produced.

[0004] The soot-containing water can be further processed using petroleum naphtha to extract the carbon from the water phase. The soot can then be extracted from the petroleum naphtha with a heavy oil. The heavy oil will then contain substantially all the entrained carbon and can be used as a feedstock for the partial oxidation reactor, thereby utilizing the energy value of the carbon. Benzene can also be used as an alternative to naphtha as an extracting agent for the carbon. After separating the carbon from the water with the benzene, the benzene is stripped off and recovered.

[0005] Another technique used to remove the unreacted or unconverted carbon is to filter the scrubbing water and to recover the carbon filter cake for further processing.

[0006] U.S. Patent No. 3,979,188 to McCallister discloses a method of concentrating the water-carbon slurry from the reactor gaseous effluent scrubbing step to about 5 to 7 percent carbon, mixing the concentrated slurry with a fuel oil and returning the carbon/oil/water mixture without vaporization to the partial oxidation reactor as a substitute for the commonly used superheated high pressure steam moderator.

[0007] U.S. Patent No. 4,699,631 to Marion also discloses a method for concentrating an aqueous dispersion of soot to produce a pumpable soot-water dispersion of about 0.55 to 4.0 weight percent of carbon soot, and recycling the soot-water dispersion to the gas feed to the partial oxidation gasifier.

[0008] U. K. Patent No 1,321,069 to Shell International Research discloses carbon soot removal by agglomerating the soot particles with a hydrocarbon oil as an auxiliary agent. The use of an auxiliary substance that renders the soot particles hydrophobic and oleophilic is also disclosed. Once formed, the agglomerated particles are physically removed using a sieve, are dried to remove residual water, and are finally recycled back to the gasifier as a reactant.

[0009] U. S. Patent No. 4,289,647 to Tippmer discloses a method for recovering carbon from the effluent gas of a gasification reaction. The gas is quenched with water to separate the unburned carbon and ash, and the heat of the effluent gas is used to produce steam. The wash water is then decanted to separate it into clear water, carbon-containing water, and ash mud. The carbon-containing water is used to produce steam to control the conversion of the ash oil in the gasification reaction.

[0010] Partial oxidation gasifiers usually operate at high conversion rates to minimize soot formation. High soot formation is undesirable due to unstable soot suspensions and to increased bulk viscosity. Greater soot formation means a lower cold gas efficiency unless the heat value of the soot is recovered.

[0011] The amount of water that can be used to scrub the soot is limited to that needed to function as a moderator in the partial oxidation gasifier as determined by a heat balance. The amount of soot generated is set by the carbon:oxygen ratio. Thus the amount of water cannot be varied to prevent excessive soot buildup. It is an object of this invention to separate the water and soot streams to allow for a variation of the quantity of quench water used to scrub the soot. The soot can be concentrated by recycling the quench water to the quench ring of the quench zone.

[0012] Ideally, the gasifier could be run at lower syngas conversion rates while maintaining a low viscosity in the soot/water mixture.

[0013] In the partial oxidation gasification process, the raw process gas exits from the reaction zone of the gasifier at a temperature in the range of 926.7 °C to 1926.7 °C (about 1700°F to about 3500°F), typically from 1093.3 °C to 1537.8 °C (about 2000°F to about 2800°F) and at a pressure of 1380 to 17,200 kPa (about 200 psia to about 2500 psia), typically from 4830 to 10,300 kPa (about 700 psia to about 1500 psia). Particulate carbon is present in the range of nil to about 20 weight percent based on the amount of carbon in the original feed.

[0014] U. S. Patent No. 4,021,366, to Robin et al., discloses that it is desirable to maintain the concentration of particulate carbon in the quench water in the range of nil to about 20 weight percent, desirably below 1.5 weight percent.
The hot raw effluent syngas stream leaving the reaction zone of the partial oxidation gasifier carries with it substantially all the particulate carbon soot produced in the reaction zone of the gasifier. The hot raw effluent syngas stream is introduced into a quench zone or chamber located below the reaction zone of the gasifier. The turbulent condition of the quench zone, caused by large volumes of syngas bubbling through the quench water present therein, helps to scrub or remove most of the soot from the syngas. The quench chamber generates quantities of soot mixed with water.

In some gasification processes, moderator in the form of steam, water or other material such as carbon dioxide is required with oil feeds. When steam is used, less oxygen is generally required and a higher cold gas efficiency is possible.

When water is used as the moderator in the gasifier, soot and water formed during the partial oxidation gasification reaction can be recycled to the gasifier, thereby minimizing or eliminating the need for soot filter cake blowdown or for a carbon extraction unit.

This invention combines the benefits of steam and water moderators by recycling soot and water into the oil feed. The water is then removed by vaporizing it at high pressure.

The simple disposal of filter cake from the filtration of quench water poses many environmental difficulties. This invention provides a novel method for utilizing soot filter cake by recycling it to the gasifier for use as a reactant.

SUMMARY OF THE INVENTION

The present invention provides a method for the recovery of elemental carbon or soot produced during the partial oxidation reaction of a hydrocarbonaceous fuel and oxygen. An effluent stream of raw synthesis gas or syngas with entrained carbon soot is produced during the partial oxidation reaction. The effluent stream is scrubbed with water to produce a stream of soot-free syngas and a stream of water contaminated with soot. The soot is removed from the water, generally by filtration or other equivalent means to form a filter cake. Most or all of the filter cake is recycled to the gasifier to serve as a reactant.

DESCRIPTION OF THE DRAWING

Fig. 1 is a schematic diagram of the process of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In accordance with the present invention, the raw syngas effluent stream containing small amounts of entrained carbon soot and small amounts of entrained mineral ash is scrubbed with water. A clean syngas stream and a scrubbing water stream containing carbon soot and mineral ash are produced.

The scrubbing water stream is filtered to remove a major portion of the carbon soot in the form of a filter cake. The filter cake typically contains about 50 to 85 % weight water, about 15 to 50 % weight carbon soot, and about 2 to 20 % weight mineral ash.

Most or all of the wet filter cake is contacted with a slipstream of oil feed to the gasifier at elevated pressure. Substantially all of the water from the filter cake is vaporized to form steam and is passed to the combustion zone of the gasifier, wherein it serves as a temperature moderator. The carbon soot and mineral ash become part of the oil slipstream to form an oil/soot/ash mixture which is then combined with the primary oil feed that is introduced into the reaction zone of the gasifier.

This invention enables the carbon soot to be completely burned in the gasifier and results in an increase in overall process efficiency. It also minimizes or eliminates the need for solid waste disposal of the filter cake, thereby eliminating or substantially reducing the associated environmental concerns and operating costs.

The operating system of the invention includes at least one lockhopper or equivalent apparatus, and can also comprise two or more lockhoppers operating in parallel, and a common knockout vessel, circulation pump, and heat exchanger.

Referring to Fig. 1, a wet carbon soot filter cake 2 usually obtained from the filtration of a syngas scrubbing water enters receiving bin 10 at ambient conditions.

The filter cake 2, can be divided into filter cake portions 4 and 6. Filter cake portion 4 can be diverted to solid waste disposal (not shown) to control the accumulation of mineral ash in the system. Filter cake portion 4 generally comprises up to about 20 weight % of the total filter cake being processed.

Filter cake portion 6 can be routed to the one or more lockhoppers that operate in parallel (not shown) with lockhopper 14.

Wet filter cake 8 exits receiving bin 10 and enters lockhopper 14 through open valve 12 under an inert atmosphere, preferably nitrogen. The entry to lockhopper 14 is surrounded by valves 16, 18, 20 and 22, which are in the closed position during the entry of wet filter cake 8 through valve 12.

When the wet filter cake occupies about 10% to about 50% of the total volume of lockhopper 14, valve 12 is closed and lockhopper 14 is pressurized to 689 to 2070 kPa (about 100 psi to about 300 psi) above the operating pressure of the partial oxidation gasifier.

Valves 22 and 16 are then opened and oil feed stream 36 enters lockhopper 14 through valve 22 to form a wet filter cake/oil feed mixture therein. As the level of the oil rises in lockhopper 14, nitrogen is displaced.
through valve 16 and through line 38 which contains a pressure control valve (not shown), and passes through line 42 and enters knockout vessel 44.

[0033] Lockhopper 14 eventually becomes filled completely with the wet filter cake/oil feed mixture which then exits through valve 16 and similarly flows through lines 38 and 42 and into the knockout vessel 44.

[0034] The pressure downstream of the control valve in line 38 is adjusted to vaporize a portion of the water so that it will remain in the vapor phase until it enters the reaction zone of the gasifier for use as a temperature moderator. Depending on the gasifier requirements, all or a portion of the water vapor plus any accompanying oil vapors can be passed to the gasifier.

[0035] The oil and water vapor mixture exits knockout vessel 44 through lines 46 and 50, and enters the reaction zone of the gasifier (not shown). The oil vapor is consumed in the partial oxidation reaction, and the water vapor helps to moderate the reaction temperature.

[0036] The more concentrated wet filter cake/oil feed mixture accumulates in knockout vessel 44 until operating level is reached, which occurs when knockout vessel 44 is about 30% to about 50% full, by volume.

[0037] Once the designated operating level is established in knockout vessel 44, lockhopper valve 18 is opened. The more concentrated wet filter cake/oil feed mixture passes through line 52, pump 54, and line 56 into heat exchanger 58, where heat is supplied to the more concentrated wet filter cake/oil feed mixture exiting as stream 60, which can then be divided into streams 62 and 64. Stream 64 flows through valve 18 into lockhopper 14. Stream 62 enters another parallel lockhopper (not shown).

[0038] Inside lockhopper 14 the more concentrated wet filter cake/oil feed 60 is mixed with the oil feed stream 36 entering through valve 22. The combined mixture of oil feed and the more concentrated wet filter cake/oil feed exits the top of lockhopper 14, through valve 16, and the pressure control valve (not shown) in line 38. Flashing occurs across the pressure control valve to produce a vapor stream of water with small amounts of oil and a drier filter cake/oil feed mixture which enter knockout vessel 44 and are separated in lines 46 and 52 as previously described.

[0039] The circulation of the drier filter cake/oil feed stream 52 from knockout vessel 44 to lockhopper 14 is continued until little additional water vapor is generated in line 46 and a substantially dry filter cake/oil feed is produced. For example, the water content is typically less than about 0.5 weight %.

[0040] The circulating pump 54 and the heat exchanger 58 are then deactivated. Lockhopper valves 16, 18, and 22 are closed, and lockhopper valve 20 is opened. The substantially dry mixture of oil feed and filter cake, which is more accurately an oil feed/particulate carbon mixture, exits lockhopper 14 through lines 66 and 70 and into the oil feed storage drum 26.

[0041] Oil feed 24 enters one side of the oil feed storage drum 26. The pressure of the oil feed varies from 2070 to 17,900 kPa (about 300 psig to about 2600 psig), preferably from 4140 to 11,000 kPa (about 600 psig to about 1600 psig). The temperature of the oil feed varies from 204.4 °C to 371.1 °C (about 400°F to about 700°F), preferably from 232.2 °C to 343.3 °C (about 450°F to about 650°F).
Claims

1. A method for the recovery and reuse of unreacted carbon soot produced by the partial oxidation reaction of a hydrocarbonaceous fuel and oxygen in a partial oxidation reactor to produce an effluent stream of synthesis gas and entrained carbon soot, comprising:

a) scrubbing the effluent stream with water to remove the entrained carbon therefrom, thereby producing a carbon soot-free synthesis gas and a stream of water and entrained carbon;

b) filtering the stream of water and entrained carbon to produce a wet filter cake of carbon soot;

c) contacting the wet filter cake with oil at a first pressure to form a first mixture of carbon soot/oil/water;

d) exposing the carbon soot/oil/water mixture to a second pressure, lower than the first pressure, to vaporize and separate a portion of the water content from the first carbon soot/oil/water mixture to thereby form a more concentrated second carbon soot/oil/water mixture;

e) recycling the more concentrated second carbon soot/oil/water mixture to steps (c) and (d) wherein essentially all of the water is removed to form a substantially water-free carbon soot/oil mixture; and

f) passing the substantially water-free carbon soot/oil mixture to a partial oxidation gasification reaction to serve as a reactant.

2. The method of claim 1, wherein all or a portion of the water vapor is used as a temperature moderator in the partial oxidation gasification reaction.

3. The method of claim 1, wherein the first pressure is 689 to 2.070 kPa (about 100 psi to about 300 psi) above the operating pressure of the partial oxidation gasification reaction.

4. The method of claim 1, wherein the second pressure is sufficient to maintain the water vapor in a vapor phase until it enters the reaction zone of the gasifier.

5. The method of claim 1, wherein step (c) is conducted in a lockhopper.

6. The method of claim 5, wherein the initial contact of the wet filter cake with the oil occurs when the wet filter cake occupies 10% to 50% of the total volume of the lockhopper.

7. The method of claim 1, wherein the separation of the water vapor in step (d) is conducted in a knock-out vessel.

8. The method of claim 7, wherein the more concentrated carbon soot/oil/water mixture is recycled from the knockout vessel when said vessel is 30% to 50% full by volume.

9. The method of claim 1, wherein the substantially water-free carbon soot/oil mixture contains less than 0.5 weight % water.

Patentansprüche

1. Verfahren für die Wiedergewinnung und Wiederverwendung von unreagiertem Kohlenstoffruß, der durch die Partialoxidationsreaktion eines kohlenwasserstoffhaltigen Brennstoffs und von Sauerstoff in einem Partialoxidationsreaktor hergestellt wird, unter Bildung eines Austrittstroms von Synthesegas und mitgerissenem Kohlenstoffruß, umfassend:

a) Waschen des Austrittstroms mit Wasser zum Entfernen des mitgerissenen Kohlenstoffes davon unter Bildung eines von Kohlenstoffrußfreien Synthesegases und eines Stroms von Wasser und mitgerissenem Kohlenstoff;

b) Filtrieren des Stroms von Wasser und mitgerissenem Kohlenstoff unter Bildung eines nassen Filterkuchens von Kohlenstoffruß;

c) Kontaktieren des nassen Filterkuchens mit Öl bei einem ersten Druck unter Bildung einer ersten Mischung von Kohlenstoffruß/Ol/Wasser;


e) Rückführen der konzentrierteren zweiten Mischung von Kohlenstoffruß/Ol/Wasser zu den Schritten (c) und (d), wobei im Wesentlichen das gesamte Wasser unter Bildung einer im Wesentlichen wasserfreien Mischung von Kohlenstoffruß/Ol entfernt wird;

f) Zuführen der im Wesentlichen wasserfreien Mischung von Kohlenstoffruß/Ol zu einer Partialoxidationsvergasungsreaktion, um als Reaktant zu dienen.
2. Methode nach Anspruch 1, wobei das gesamte oder ein Teil des Wasserdampfs als Temperaturmoderator bei der Partialoxidationsvergasungsreaktion verwendet wird.

3. Methode nach Anspruch 1, wobei der erste Druck 689 bis 2070 kPa (ca. 100 psi bis ca. 300 psi) über dem Arbeitsdruck der Partialoxidationsvergasungsreaktion liegt.

4. Methode nach Anspruch 1, wobei der zweite Druck ausreicht, um den Wasserdampf in einer Dampfphase zu halten, bis er in die Reaktionszone des Vergasers eintritt.

5. Methode nach Anspruch 1, wobei der Schritt (c) in einem Schließertrichter durchgeführt wird.

6. Methode nach Anspruch 5, wobei der anfängliche Kontakt des nassen Filterkuchens mit dem Öl dann stattfindet, wenn der nasse Filterkuchen 10 % bis 50 % des Gesamtvolumens des Schließertrichters einnimmt.

7. Methode nach Anspruch 1, wobei die Abtrennung des Wasserdampfs in Schritt (d) in einem Ausstoßgefäß stattfindet.

8. Methode nach Anspruch 7, wobei die konzentrierte Mischung von Kohlenstoffruß/Öl/Wasser von dem Ausstoßgefäß rückgeführt wird, wenn das Gefäß 30 % bis 50 %, auf das Volumen bezogen, gefüllt ist.

9. Methode nach Anspruch 1, wobei die im Wesentlichen wasserfreie Mischung von Kohlenstoffruß/Öl weniger als 0,5 Gew.-% Wasser enthält.

Revendications

1. Procédé en vue de la récupération et de la réutilisation de suie n’ayant pas réagi, produite par la réaction d’oxydation partielle d’un combustible hydrocarboné et d’oxygène dans une réaction d’oxydation partielle pour produire un courant effluent de gaz de synthèse et de suie entraînée, comprenant :
   a) le lavage du courant effluent à l’aide d’eau pour en éliminer le carbone entraîné, en produit ainsi un gaz de synthèse exempt de suie et un courant d’eau et de carbone entraîné ;
   b) le filtrage du courant d’eau et du carbone entraîné pour produire un gâteau humide de filtre de suie ;
   c) la mise en contact du gâteau humide de filtre de suie avec de l’huile à une première pression pour former un premier mélange de suie/île/d’eau ;
   d) l’exposition du mélange de suie/île/d’eau à une deuxième pression, inférieure à la première pression, pour évaporer et séparer une portion de la teneur en eau du premier mélange de suie/île/d’eau pour former ainsi un mélange plus concentré de suie/île/d’eau ;
   e) le recyclage du deuxième mélange plus concentré de suie/île/d’eau aux étapes (c) et (d), dans lesquelles, pour l’essentiel, la totalité de l’eau est éliminée pour former un mélange de suie/île, substantiellement exempt d’eau ; et
   f) le passage du mélange de suie/île substantiellement exempt d’eau à une réaction de gazéification par oxydation partielle pour servir en tant que réactif.

2. Procédé selon la revendication 1, dans lequel la totalité ou une portion de la vapeur d’eau est utilisée en tant qu’agent modérateur de température dans la réaction de gazéification par oxydation partielle.

3. Procédé selon la revendication 1, dans laquelle la première pression est de 689 à 2070 kPa (d’environ 100 livres par pouce au carré à environ 300 livres par pouce au carré) au-dessus de la pression de fonctionnement de la réaction de gazéification par oxydation partielle.

4. Procédé selon la revendication 1, dans lequel la deuxième pression est suffisante à maintenir la vapeur d’eau dans une phase vapeur jusqu’à ce qu’elle entre dans la zone de réaction du dispositif de gazéification.

5. Procédé selon la revendication 1, dans lequel l’étape (c) est effectuée dans une trémie à sas.

6. Procédé selon la revendication 5, dans lequel le contact initial du gâteau humide de filtre avec l’huile se produit lorsque le gâteau humide de filtre occupe de 10 à 50 % du volume total de la trémie à sas.

7. Procédé selon la revendication 1, dans lequel la séparation de la vapeur d’eau dans l’étape (d) est effectuée dans une cuve d’éjection.

8. Procédé selon la revendication 7, dans lequel le mélange plus concentré de suie/île/d’eau est recyclé hors de la cuve d’éjection lorsque ladite cuve est pleine à raison de 30 % à 50 % en volume.

9. Procédé selon la revendication 1, dans lequel le mélange de suie/île, substantiellement exempt d’eau, contient moins de 0,5 % en poids d’eau.