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(54) **Process for producing coke with a low volatile carbonaceous matter content.**

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EP 0 454 425 B1

Description

The present invention relates to an improved process for forming coke with a low volatile carbonaceous matter (VCM) content.

Processes for forming coke from petroleum hydrocarbons are well-known. See, for example, U.S. Patent Nos. 3,745,110 and 3,836,434; the disclosures of which are incorporated herein by reference. Such processes involve heating certain petroleum hydrocarbon streams to elevated temperatures, for example 496°C (925°)-524°C 975°F), and rapidly running the hot hydrocarbons into the bottom of a relatively quiescent chamber known as a coking drum. As the hydrocarbons are charged into the coking drum, they undergo coking, i.e., they undergo a chemical change from a liquid to a solid.

When charging of the coking drum with petroleum hydrocarbons is completed, it is customary to introduce steam into the bottom of the coking drum. This procedure, which is referred to as steam stripping, drives off non-coked hydrocarbons, i.e., portions of the hydrocarbon feed which have not become a carbonaceous solid. In addition, steam stripping provides initial cooling of the very hot mass of coke in the coking drum. After steam stripping, the coke is further cooled to a relatively low temperature of about 93°C (200°F) or less so that it can be safely removed from the coking drum. The cooling is accomplished by charging steam and water into the bottom of the coking drum. Care must be taken to adjust the water flow rate during water cooling to prevent high pressures from developing at the coke drum inlet.

When the water cooling operation is completed, the coking drum is ready for emptying. This is accomplished by removing covering plates called heads, located at the top and bottom of the coking drum and breaking the hardened coke into chunks. Break-up of the coke is normally accomplished by means of high pressure water drills which direct jets of high pressure water into the coke. The chunks of coke so formed fall through the bottom of the coking drum to railcars or other suitable means of transportation.

As an alternative to steam stripping, U.S. Pat. No. 4,547,284 discloses that a portion of the VCM can be converted to coke by passing a heated non-coking vapor through the contents of the drum after the coker drum has been taken off stream, i.e., the residuum feed has been switched to the other coke drum. The non-coking vapor is introduced at a temperature above the coke temperature to increase the coke temperature and facilitate reacting of the VCM. This requires additional energy input and increases cycle time, thereby decreasing the productivity of the coker.

Generally, coke buyers prefer coke with a low, consistent volatile carbonaceous matter (VCM) content. However, "green" coke, as it is removed from the coking drums, usually contains high amounts of tar-like VCM. VCM is especially high in the coke found in the upper portion of the coke drum which has experienced the shortest reaction time. Customarily, this "green" coke is subjected to calcination at elevated temperatures to reduce the VCM and produce a finished petroleum coke. However, coke with a high VCM content often undergoes undesirable "popcorning" i.e., sudden expansion when subjected to higher calcination temperatures.

Accordingly, it is an object of the present invention to provide an improved method for preparing "green" coke with a low volatile carbonaceous matter content without increasing cycle time or furnace fuel demand.

SUMMARY OF THE INVENTION

It is a primary objective of this invention to provide an efficient process for the production of coke having a reduced VCM content. Additional objects and advantages of this invention will be obvious from the description, examples, and appended claims.

The foregoing objective is accomplished by carrying out the coking of a petroleum hydrocarbon stream in a coking drum. Generally, the hydrocarbon is a high boiling petroleum residuum.

The high boiling petroleum hydrocarbon residuum is heated and introduced as a feedstock to a coke drum to form coke and overhead vapors. The overhead vapors escape through the top of the coke drum and are passed to a bubble tower. After the drum is filled with porous solid coke, a liquid light hydrocarbon stream is introduced into the bottom of the coking drum at a temperature below that of the coke in the drum. The light hydrocarbon stream functions to reduce the volatile carbonaceous material in the coke as it passes through the drum. The light hydrocarbon stream extracts a portion of the VCM and the mixture passes through the coking drum to an overhead outlet and subsequently to the bubble tower. Following the introduction of the light hydrocarbon stream, the coke can be optionally steam stripped or stripped with an inert stream. Finally, the coke is water quenched and cut as is known in the art.

A superior grade coke is obtained because the VCM content of the coke is reduced below the level typically achieved with steam stripping alone. In addition, the VCM remaining in the coke is more uniformly dispersed throughout the coke, i.e., the coke at the top of the drum is more similar in VCM content to the coke at the bottom of the drum. The light hydrocarbon stream, also functions to reduce the coke temperature, therefore cycle time is not increased.

The advantages of this process arise because the light hydrocarbon stream is readily available at refineries and has a much greater affinity for the tar-like VCM found in the coke than does steam. Accordingly, greater amounts of VCM are removed from the coke and cooling of the coke is still effectively accomplished. In addition, the remaining VCM is more consistently distributed. Another advantage is that bubble tower operation is more stable because the thermal upset caused by steam is avoided. Furthermore, overall cycle time is not extended by injecting a heated light hydrocarbon vapor to raise coke drum temperature. In fact, introduction of a liquid light hydrocarbon stream cools the coke more effectively than steam stripping. This occurs because the liquid light hydrocarbon stream removes heat from the coke bed during its vaporization.

The figure described below is a simplified schematic representation of a flow diagram for effecting the process of the present invention, wherein superior grade coke is produced.

Reference will now be made in detail to a preferred embodiment of the present invention. While the inventive process will be described in connection with a preferred procedure, it will be understood that it is not intended to limit the invention to that procedure. On the contrary it is intended to cover all alternatives, modifications and equivalents as may be included within the spirit and scope of the invention defined by the appended claims.

Referring now to Figure 1, a feed which is generally a petroleum residuum, e.g., crude oil vacuum bottoms, is fed through line 1 to bubble tower 3 where it is stripped. The coke drum overhead vapors entering through line 11 provide the heat for fractionation. The resultant tower bottoms consisting of condensed recycle from the coking operation and all but the low boiling fractions of the regular coker feed is passed through line 5 to the fired heater 7. The coker charge is heated to a temperature sufficient to produce the coking reaction and is passed through line 8 into one of the coke drums 9A or 9B. One of the coking drums is "on-line" being filled while the second drum is "off-line" being stripped, cooled, and emptied. Access to the drums is controlled by valves 12A and 12B. Overhead vapors from the coke drums exit via line 11 and return to the bubble tower 3.

In general, following the drum filling cycle, the bottom of the coke drum is much hotter than the top of the drum, for example about 482°C (900°F), and about 441°C (825°F) respectively. In the process of the prior art, steam is introduced into the bottom of the drum at about 177°C (350°F). The steam cools the hot coke bed and sweeps some VCM out of the bed through an overhead vapor outlet leading to a bubble tower. While the steam is being introduced, a second drum is placed "on-line" to receive the coker feedstock. Since the second coke drum is relatively cool and empty, the quantity of vapors exiting the top is much lower than the steady state value. This decrease in the amount of hot vapor entering the bubble tower upsets the heat balance and decreases the effectiveness of the bubble tower.

According to the present invention, at the point of the cycle where steam is normally introduced, a light hydrocarbon stream is introduced as an alternative, or in conjunction with steam. In the process of the present invention, the light hydrocarbon will be comprised of at least hydrogen and carbon. Furthermore, the light hydrocarbon stream is comprised largely of C_3 to C_{30} hydrocarbon molecules. Preferably, the stream consists largely of C_5 to C_{20} hydrocarbon molecules. Due to its higher vapor density, greater weights per period of time of light hydrocarbon can be passed through the drum than steam, further facilitating VCM removal. The light hydrocarbon stream should be introduced at a temperature lower than the coke temperature in the drum. Furthermore, the light hydrocarbon stream should be introduced at a temperature below its boiling range, i.e., substantially as a liquid at coke drum inlet pressure. Any hydrocarbon stream with a boiling range below the coke temperature can be used. Preferably, the light hydrocarbon has a final boiling point less than about 482°C (900°F). More preferably, the final boiling point is less than about 316°C (600°F). Blends of light hydrocarbons and/or steam are also envisioned. Preferably, the light hydrocarbon stream has a limited coking potential. The preferred light hydrocarbons are naphtha, kerosene, or light gas oil. More preferably, the light hydrocarbon is naptha or kerosene.

With regard to Figure 1, kerosene is introduced through line 13. Valves 10A and 10B direct flow into the filled "off-line" drum. The kerosene is introduced at a temperature below its boiling point. Preferably the kerosene is below about 232°C (450°F). Therefore the kerosene serves to extract heat from the coke as did steam in the prior art process. Accordingly, cycle time is not increased. In fact, better heat removal within the coke drum is achieved with light hydrocarbons rather than steam due to the energy necessary for the vaporization of the light hydrocarbon stream. Accordingly, the kerosene transfers more heat from the lower portion of the coke drum to the upper portion of the coke drum, thereby increasing the coking activity of the top portion which has been subjected to coking reaction temperatures for the shortest period of time.

In addition, the kerosene has a higher affinity for the tar-like VCM than steam and will effectively strip this material from the product coke by extracting the VCM into the gas phase. Without being bound by theory, it is also believed that the light hydrocarbons, because they are very soluble in the VCM, cause swelling of the VCM resulting in VCM being pushed out of micro-pores and into the macro-pores and channels increasing the accessibility of the solvent flow. Furthermore, the light hydrocarbon reduces the viscosity of the VCM, making it more mobile.

The hot light hydrocarbon routed back to the bubble tower through line 11, carrying the VCM will function to stabilize the thermal requirements of the column during the "on-line" swing from drum 9A to 9B. As stated above, when a filled drum is taken "off-line", the next "on-line" drum initially produces less overhead heat and vapor. In addition, the light hydrocarbon is fully miscible with the bubble tower contents, in contrast to steam, therefore it does not negatively effect the bubble tower operation.

The VCM solubilized by the kerosene can be collected from the bubble tower as usable hydrocarbons which is a significant economical advantage. The kerosene can be recovered in the bubble tower and recycled through line 13 to maintain the process.

Although stripping of the coke bed with a light hydrocarbon can eliminate the need for steam stripping, it is possible to accompany the light hydrocarbon stripping with steam stripping or to subsequently steam strip.

Lines 15, 17, 19 and 21 are the recovery lines for various product fractions from the bubble tower. The bubble tower aids recovery of products such as heavy coker gas oil (line 21), a light coker gas oil (line 19), kerosene (line 13), naphtha (line 17) and gas (line 15).

The following example is illustrative of a specific comparison of stripping with a light hydrocarbon as opposed to inert solvents.

Example 1. Coke which had previously been steam stripped, resulting in a 13.1 weight percent VCM content, was treated in a 150 cc. microreactor at 454°C (850°F) and a pressure of 272.4 kPa (25 p.s.i.g.) with solvents consisting of nitrogen, coker naphtha, and coker kerosene. The light hydrocarbon solvents resulted in much greater reduction of coke VCM.

SOLVENT STRIPPING OF COKE

Experimental Results:

Feed = Coke (13.1 wt% VCM)
Temp = 454°C (850°F)
Pressure = 272.4 kPa (25 psig)

Solvent	Product VCM
Nitrogen	13.0 wt%
Coker Naphtha	7.3
Coker Kerosene	7.6

Thus it is apparent that there has been provided, in accordance with the invention, a process that fully satisfies the objects, aims and advantages set forth above. While the invention has been described in conjunction with specific embodiments thereof, it is evident that many alternatives, modifications, and variations will be apparent to those skilled in the art in light of the foregoing description. Accordingly, it is intended to embrace all such alternatives, modifications, and variations as fall within the spirit and broad scope within the appended claims.

Claims

1. A process for preparing coke having a low volatile carbonaceous matter content from a petroleum feedstock comprising:
   (a) heating and introducing a petroleum feedstock to a coke drum to form coke and overhead vapors;
   (b) passing a light hydrocarbon stream through said coke, wherein said light hydrocarbon stream enters said coke drum in a substantially liquid phase; and
   (c) removing said light hydrocarbon containing at least a portion of the volatile carbonaceous matter from said coke drum.

2. A process as claimed in claim 1, wherein said overhead vapors of step (a) and said light hydrocarbon stream of step (c) are passed to a bubble tower.

3. A process as claimed in claim 1 or claim 2 wherein said petroleum feedstock is introduced at 454°C (850°F) or above.

4. A process as claimed in any one of the preceding claims wherein said light hydrocarbon stream has a boiling range below the temperature of said coke.

5. A process as claimed in claim 4, wherein said light hydrocarbon stream has a final boiling point less than about 482°C (900°F).

6. A process as claimed in claim 5, wherein said light hydrocarbon stream has a final boiling point less than about 316°C (600°F).

7. A process as claimed in any one of the preceding claims wherein said light hydrocarbon stream is selected from the group consisting of naphtha, kerosene, light gas oil and blends thereof.

8. A process as claimed in claim 7, wherein said light hydrocarbon stream is selected from the group consisting of naphtha and kerosene.

9. A process as claimed in any one of the preceding claims wherein said passing of said light hydrocarbon stream of step (b) is followed by steam stripping.

10. A process as claimed in any one of the preceding claims wherein said light hydrocarbon stream of step (b) is a blend of light hydrocarbon and steam.

11. A process as claimed in claim 2, wherein said light hydrocarbon is recycled through said bubble tower back to said coke drum.

12. A process as claimed in any one of the preceding claims wherein said light hydrocarbon stream of step (b) is a blend of light hydrocarbon, steam and any inert additive.

Patentansprüche

1. Verfahren zur Herstellung von Koks mit einem geringen Gehalt an flüchtigem kohlenstoffhaltigem Material aus einem Erdölausgangsmaterial, umfassend:
   (a) Erwärmen und Einleiten eines Erdölausgangsmaterials in eine Kokereitrommel zur Bildung von Koks und Überkopfdämpfen;
   (b) Durchleiten eines Leichtkohlenwasserstoffstroms durch den Koks, wobei der Leichtkohlenwasserstoffstrom in die Kokereitrommel in einer im wesentlichen flüssigen Phase eintritt, und
   (c) Entfernen des mindestens einen Teil des flüchtigen kohlenstoffhaltigen Materials enthaltenden Leichtkohlenwasserstoffs aus der Kokereitrommel.

2. Verfahren nach Anspruch 1, wobei die Überkopfdämpfe der Stufe (a) und der Leichtkohlenwasserstoffstrom der Stufe (c) zu einem Fraktionierturm geleitet werden.

3. Verfahren nach Anspruch 1 oder Anspruch 2, wobei das Erdölausgangsmaterial bei 454°C (850°F) oder darüber eingeleitet wird.

4. Verfahren nach einem der vorherigen Ansprüche, wobei der Leichtkohlenwasserstoffstrom einen Siedebereich unter der Temperatur des Kokses aufweist.

5. Verfahren nach Anspruch 4, wobei der Leichkohlenwasserstoffstrom einen Endsiedepunkt von weniger als etwa 482°C (900°F) aufweist.

6. Verfahren nach Anspruch 5, wobei der Leichtkohlenwasserstoffstrom einen Endsiedepunkt von weniger als etwa 316°C (600°F) aufweist.

7. Verfahren nach einem der vorherigen Ansprüche, wobei der Leichtkohlenwasserstoffstrom aus der Gruppe Naphtha, Kerosin, Leichtgasöl und Mischungen davon ausgewählt wird.

8. Verfahren nach Anspruch 7, wobei der Leichtkohlenwasserstoffstrom aus der Gruppe Naphtha und Kerosin ausgewählt wird.

9. Verfahren nach einem der vorhergehenden Ansprüche, wobei dem Durchleiten des Leichtkohlenwasserstoffstroms der Stufe (b) ein Dampfabstreifen folgt.

10. Verfahren nach einem der vorhergehenden Ansprüche, wobei der Leichkohlenwasserstoffstrom der Stufe (b) aus einer Mischung aus Leichtkohlenwasserstoff und Dampf besteht.

11. Verfahren nach Anspruch 2, wobei der Leichtkohlenwasserstoff durch den Fraktionierturm zu der Verkokungstrommel zurückgeführt wird.

12. Verfahren nach einem der vorhergehenden Ansprüche, wobei der Leichtkohlenwasserstoffstrom der Stufe (b) aus einer Mischung von Leichtkohlenwasserstoff, Dampf und irgendeinem inerten Zusatzstoff besteht.

Revendications

1. Procédé pour préparer du coke ayant une faible teneur en matière carbonée volatile à partir d'une charge d'alimentation de pétrole comprenant les opérations consistant:
   (a) à chauffer et à introduire la charge d'alimentation de pétrole à un réacteur de coke pour former du coke et des vapeurs de tête;
   (b) à faire passer un courant d'hydrocarbure léger à travers ledit coke, dans lequel ledit courant d'hydrocarbure léger pénètre dans ledit réacteur de coke en phase pratiquement liquide; et
   (c) à retirer ledit hydrocarbure léger contenant au moins une partie de la matière carbonée volatile dudit réacteur de coke;

2. Procédé selon la revendication 1, dans lequel on fait passer les vapeurs de tête de l'étape (a) et le courant d'hydrocarbure léger de l'étape (c) dans une colonne à plateaux.

3. Procédé selon la revendication 1, dans lequel on introduit ladite charge d'alimentation de pétrole à une température de 454°C (850°F) ou au-dessus.

4. Procédé selon la revendication 4, dans lequel ledit courant d'hydrocarbure léger a un point d'ébullition final inférieur à la température dudit coke.

5. Procédé selon la revendication 4, dans lequel ledit courant d'hydrocarbure léger possède un point d'ébullition final de 482°C (900°F).

6. Procédé selon la revendication 5, dans lequel ledit courant d'hydrocarbure léger a un point d'ébullition final inférieur à environ 316°C (600°F).

7. Procédé selon l'une quelconque des revendications précédentes, dans lequel on choisit ledit courant d'hydrocarbure léger dans le groupe constitué par le naphta, le kérosène, le gazole léger et leurs mélanges.

8. Procédé selon la revendication 7, dans lequel on choisit ledit courant d'hydrocarbure léger dans le groupe constitué par le naphta et le kérosène.

9. Procédé selon l'une quelconque des revendications précédentes dans lequel ledit passage dudit courant d'hydrocarbure léger de l'étape (b) est suivi par un dégazolinage par entraînement à la vapeur d'eau.

10. Procédé selon l'une quelconque des revendications précédentes, dans lequel ledit courant d'hydrocarbure léger de l'étape (b) est un mélange d'hydrocarbure léger et de vapeur d'eau.

11. Procédé selon la revendication 2, dans lequel ledit hydrocarbure léger est recyclé à travers ladite colonne à plateaux et renvoyés au réacteur de coke.

12. Procédé selon l'une quelconque des revendications précédentes, dans lequel ledit courant d'hydrocarbure léger de l'étape (b) est un mélange d'hydrocarbure léger, de vapeur d'eau et de tout additif inerte.

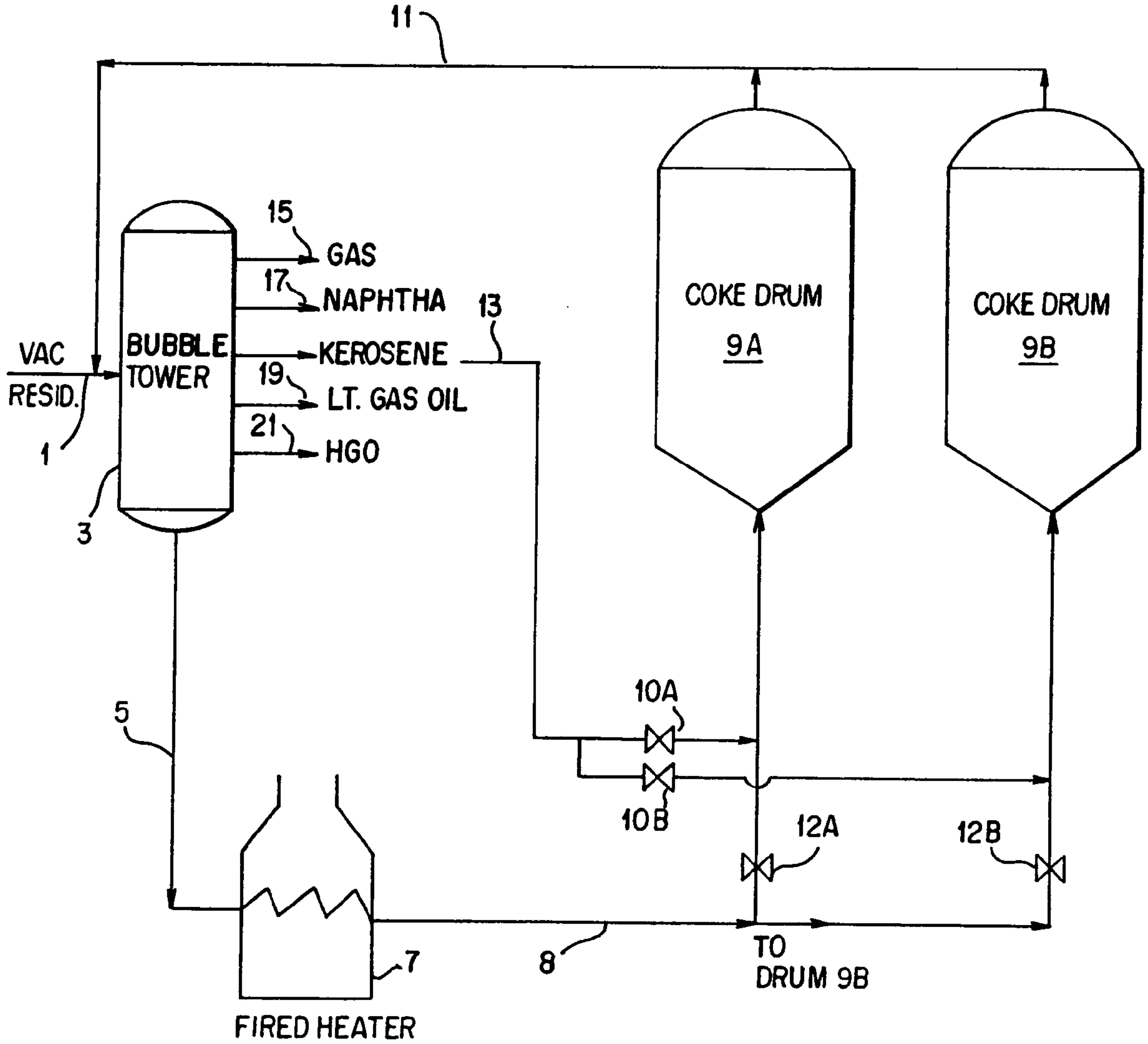
11
15
GAS
17
NAPHTHA
13
KEROSENE
19
LT. GAS OIL
21
HGO
VAC
RESID.
1
BUBBLE
TOWER
3
COKE DRUM
9A
COKE DRUM
9B
5
10A
10B
12A
12B
7
8
TO
DRUM 9B
FIRED HEATER

FIG. 1