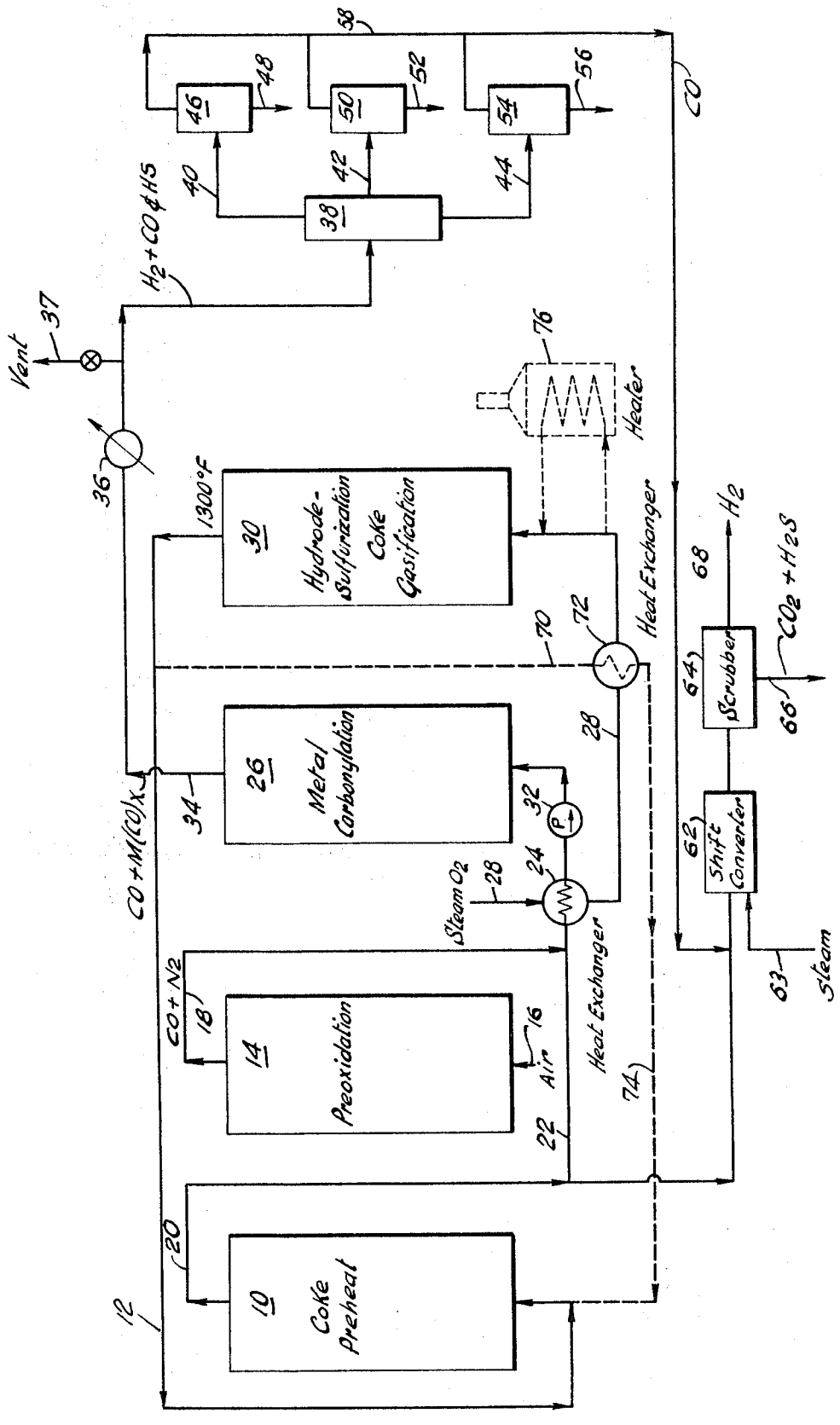
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PURIFICATION OF PETROLEUM COKE

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PURIFICATION OF PETROLEUM COKE

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ABSTRACT OF THE DISCLOSURE

Purification of petroleum coke high in sulfur and containing metallic impurities by passing an excess of synthesis gas in contact with the preoxidized coke at a temperature and pressure at which the carbon monoxide of the synthesis gas is caused to combine with the metals, under the catalytic effect of the sulfur in the coke, to form gasiform metal carbonyls which are readily separated. The resulting synthesis gas is then used to hydrodesulfurize the coke under appropriate conditions.

The present invention relates to the upgrading and purification of petroleum coke by the removal of those typical impurities and contaminants which characteristically limit the use of this product in desirable specialty applications.

BACKGROUND OF INVENTION

The requirement for calcined coke for metallurgical uses as, for example, in the manufacture of electrodes for use in the aluminum industry imposes requirements not ordinarily met by untreated petroleum coke. Such cokes, whether made by the fluid or by the delayed coking process, or by other conventional methods, tend to concentrate undesirable constituents of the petroleum, such as residual sulfur and metals such as iron, nickel and vanadium.

This follows from the fact that coking itself offers a desirable means for obtaining valuable fractions from rather low grade residua. Moreover the process of coking itself inherently tends to concentrate these undesirable constituents of the residual oil in the coke.

It has been proposed to remove sulfur from petroleum coke by high temperature hydrogenation. For example, Industrial Engineering Chemistry, September 1959, Volume 51, No. 9, page 1027 proposes the hydrodesulfurization of coke at elevated temperatures in the vicinity of 1300° F. and at high hydrogen rates following a limited, low temperature preoxidation treatment which is said to open up the structure of the coke, and to vastly increase the surface area so as to materially promote the facilitate the hydrodesulfurization reaction. This treatment, however, fails to materially dispose of the metal contaminants which are just as seriously objectionable.

PRESENT INVENTION

The present invention contemplates purification, and specifically a substantial reduction in the level of both the aforementioned sulfur and metallic impurities in a high sulfur coke by successive treatments with synthesis gas, first to remove metals as volatile carbonyls and second, to effect hydrodesulfurization.

More specifically the invention proposes to preheat and preoxidize the petroleum coke followed by intimate contact of the pretreated coke with a stream of synthesis gas rich in carbon monoxide in a first stage maintained under conditions of temperature and pressure favorable to the carbonylation of the aforementionel metal impurities and in the presence of the high sulfur contaminant as a carbonylation catalyst.

Thereafter in a subsequent or second stage treatment the coke is again subjected to intimate contact with a stream of synthesis gas at an elevated hydrodesulfurization temperature to effect removal of sulfur from the coke as gaseous hydrogen sulfide.

Thus a critical feature of the present invention involves the carbonylation of the metal impurities in the presence of undesulfurized coke, the sulfur or sulfur compounds of which are known to catalyze the direct combination of metals with carbon monoxide to form carbonyl compounds thereof. As a result the invention contemplates acceleration of the carbonylation reaction to a point of improved commercial attractiveness.

The present invention also has a number of important prospective advantages. First it operates upon a stream of synthesis gas which is tending to become an important and necessary requirement for refineries with increasing hydrogen requirements.

Moreover it provides a large excess of treating gas favorable to a thorough-going desulfurization and demetallization of the coke without materially (if at all) penalizing the final yield of synthesis gas which goes to the refinery. Further, the invention provides a means for the production of iron, nickel and vanadium in a highly specialized form, desirable for particular purposes—namely as so-called high grade Raney metal.

Finally calcination of the coke becomes an incidental feature so that this further treatment is unnecessary.

DEFINITIONS

The term "synthesis gas" as used herein means gaseous mixtures consisting essentially of molecular hydrogen and carbon monoxide, such as are produced either by partial oxidation or steam reforming of hydrocarbons including coke gasification.

The term "high sulfur coke" means a petroleum coke having a sulfur content of at least 4% and typically in the range of about 5–8% or higher.

The terms "desulfurization" and "hydrodesulfurization" as employed herein are intended to include partial desulfurization or reduction of the total sulfur content as well as substantially complete removal of sulfur from the coke. Likewise the words "demetallization" or "carbonylation" as used herein are concerned with partial as well as entire removal of the metal, since it is understood by those skilled in the art that the foregoing processes all desirably accomplish a reduction in impurity content of the material undergoing treatment but seldom, if ever, accomplish complete removal of the material.

DETAILS OF PRESENT INVENTION

In the metal carbonylation step the coke is intimately and directly contacted with gas rich in carbon monoxide at a temperature in the range of approximately 275–430° F. and preferably in an amount materially in excess of the amount required stoichiometrically for reaction with all of the metals contained in the coke.

Inasmuch as the reaction is favored by pressure, the invention proposes conducting this step, at least, at pressures above atmospheric but within the range of pressure at which the product metal carbonyl remain in the gasiform or volatile phase and thus are free to pass off and separate from the coke.

In specific terms the pressures in the generator are preferably above atmospheric and advantageously may be within the range of 450–750 p.s.i.g. and, depending upon the content and disposition of the metallic impurities, can be raised as high as 1,000 p.s.i.g.

The hydrodesulfurization of the coke is conducted at temperatures of about 1300–1600° F., preferably around 1300° F. Alternatively the hydrodesulfurization may be conducted simultaneously with gasification of coke at temperatures, for example, of 1300–1800° F. or higher. By gasification is meant the reaction of a portion of the coke

with molecular oxygen and preferably steam to produce synthesis gas.

The accompanying drawing is a diagrammatic representation of a series of process steps illustrating one preferred embodiment of the invention.

In referring to the drawing it is to be specifically understood that it is not intended to represent a continuous process but rather a batch operation in which each of the indicated steps signifies a separate and successive process step, progressing from left to right as viewed in the figure. Accordingly, therefore, in practice, the invention contemplates the successive switching of flow (which is not shown but which is thoroughly understood by those skilled in the art) so that each batch of coke successively placed in each succeeding process step as the preceding process step is completed.

First therefore, in preheating step **10** a loose mass of particulate coke is continuously contacted by a hot stream of synthesis gas from the hydrodesulfurization step to be hereinafter described in more detail. The hot synthesis gas is introduced into the coke preheater **10** via line **12** at a temperature, for example, in the neighborhood of 1300° F., gradually bringing the coke temperature up to the region of 600–800° F., preferably about 650–700° F.

To facilitate uniform heating of the mass and also in order to accelerate and facilitate the rates of the reactions to be hereinafter carried out, the coke mass in this and the succeeding steps, preferably takes the form of a fluidized bed of relatively fine granules, for example, from 35 to 60 mesh or finer. Actually uniformity and control of the bed temperature may be advantageously effected by maintaining a dense fluid phase of coke particles. This, as is known, is effected by controlling the distribution and velocity of the incoming gas.

With the preheat temperature raised to 700° F. for example, the coke is now, in the second step indicated by the reference numeral **14**, subjected to controlled preoxidation by an upflow of molecular oxygen or air introduced as at **16**. Preoxidation, as previously intimated, calls for carefully limited low temperature oxidation, below 1100° F. and preferably in the neighborhood of 650° F., such that only from about 6 to 9% of the coke is consumed. One physical result is a sharp increase in the effective surface area of the coke which rises typically from about 5 to 200 square meters per gram and normally in the region of 400–500 square meters per gram. While this does not appear to be the sole or exclusive source of improved reaction rates which have been observed, it is one apparent factor which enables conducting subsequent chemical reactions at improved rates and further toward completion.

The effluent gases from the preoxidation step withdrawn through pipe **18** therefore consist essentially of carbon monoxide and the unaltered nitrogen from the original feed of air. This stream may be discarded, or can be mixed with the effluent gas from the coke preheater in pipe **20**, which, as previously indicated, is essentially synthesis gas containing hydrogen sulfide at a temperature in the neighborhood of 700° F. To this end, the flow in pipe **20** may be split as shown, a part passing into pipe **22** which receives the effluent from pipe **18** and flows directly into heat exchanger **24**. Exchanger **24** performs the function of lowering somewhat the temperature of the gas in line **22** to a range effective for the carbonylation step **26**, at the same time preheating the feed to the final stage of hydrodesulfurization reactor **30**.

Accordingly, in the carbonylation step **26** a stream of synthesis gas, largely carbon monoxide, is fed through line **22** at a temperature of 275–430° F., preferably 400–430° F. as maintained by exchanger **24**. As previously stated, the reaction bed may vary from a loose particulate mass to a dense fluid phase supplied with an ample excess of carbon monoxide over and above the stoichiometric quantity required to react with the metals. Advantageously

pressure pump **32** may be employed to hold step **26** at a substantial pressure, for example, up to about 1,000 p.s.i.g., but preferably from 450–750 p.s.i.g.

The fourth or hydrodesulfurization step indicated by the numeral **30** involves a combined or coincidental coke gasification which simultaneously produces the hot synthesis gas by a self supporting reaction of continuously preheated stream of steam and oxygen introduced through line **28** to heat exchanger **24** where it is preheated by exchange with gas from the coke preheater to the maximum possible extent, as for example, to about 700° F.

Preferably the gas feed to the gasification step uses either substantially pure molecular oxygen or oxygen enriched air. In any event, the reaction product of the coke gasification comprises synthesis gas rich in hot, nascent hydrogen at a temperature of about 1300–1800° F., effective to convert the elemental or combined sulfur of the coke into gaseous hydrogen sulfide. Accordingly therefore step **30** results in the contaminant sulfur passing off via conduit **12** as a stream which comprises molecular hydrogen, carbon monoxide and hydrogen sulfide.

The effluent from reaction **26** passes off by way of pipe **34** as a mixture of carbon monoxide and gasiform metal carbonyls together with molecular hydrogen and some hydrogen sulfide.

These proceed through cooling exchanger **36** to separator **38**, which functions in known manner to deliver nickel carbonyl as at **40**, iron carbonyl as at **42** and vanadium carbonyl as at **44**.

Pure carbonyl metal is produced from the metal carbonyls by raising the temperature of the carbonyl compound above is decomposition point. Therefore in reactor **46** nickel carbonyl decomposes and relatively pure Raney nickel is delivered as at **48**.

By the same token reactor **50** provides for decomposition of iron pentacarbonyl and delivery of a pure grade of Raney iron at **52**. Furthermore the sublimed vapor of vanadium, hexacarbonyl introduced through line **44** is, in reactor **54**, broken down into elemental vanadium which is delivered as at **56**.

The carbon monoxide liberated as a result of these decompositions, together with associated molecular hydrogen, passes into manifold **58** from which it flows into line **60** where it is combined with excess synthesis gas from the coke preheater and delivered for further processing as at **62**.

For example, the excess gas may be reacted with steam in shift converter **62** to form additional hydrogen and carbon dioxide, which latter material (together with contained hydrogen sulfide) may be, in turn, separated in absorption unit **64** and discharged by line **66**. Accordingly a pure stream of hydrogen is made available, via line **68**, for hydrorefining or any of the vast number of refinery processes using hydrogen.

The present invention therefore proposes preoxidation of a high sulfur coke to open up its structure and facilitate subsequent reaction, followed by carbonylation of the metallic impurities under the influence of catalytic sulfur, followed, in turn, by hydrodesulfurization of the coke.

Other factors which are expected to favor reasonably good rates of reaction are that hydrodesulfurization may be carried out with nascent synthesis gas acting upon coke which has been previously conditioned not only by the step of preoxidation but also carbonylation, both of which tend to open up the structure of the coke to improved contact by the gas. The hot effluent synthesis gas now containing hydrogen sulfide imparts a portion of its sensible heat to the incoming coke and thereafter is used at least in part to effect a carbonylation of the metal after first being reduced in temperature to a suitable temperature range. Furthermore the effluent carbon monoxide of the preoxidation step may supplement the synthesis gas by a mixture therewith.

The net result therefore is a reasonably balanced and integrated system whereby the purification steps can be

effected at enhanced rates of reaction and in the presence of excess quantities of gas which are advantageous in promoting reaction at rates and under conditions which may be commercially attractive.

A modification of the foregoing embodiment contemplates introduction of synthesis gas to the hydrodesulfurization step via pipe **28** and from any convenient source not shown, as, for example, a partial oxygen generator or a steam reformer. Inasmuch as the hydrodesulfurization reaction is no longer thermally self-supporting, the system is modified in accordance with the dotted line conduit **70** which conducts hot effluent at, for example, 1300° F. from the hydrodesulfurization unit to a second exchanger **72** which supplements the preheat of the synthesis gas feed to the hydrodesulfurization step. The effluent heating gas from the exchanger thence passes on via line **74** to coke preheat. Further thermal support for the hydrodesulfurization reaction is provided by the supplemental heating furnace **76** shown in dotted lines, which continuously maintains the hydrodesulfurization unit at a temperature in the neighborhood of 1300–1400° F. while contact is preferably in the dense fluid phase, to effect efficient desulfurization of the coke.

We claim:

1. In the purification of a high sulfur containing petroleum coke, which also contains objectionable proportions of metals such as nickel, iron and vanadium, to effect desulfurization, demetallization and calcination thereof to form metallurgical grade coke, the steps which comprise

preoxidizing said coke at a temperature in the region of 650–850° F. to effect a substantial increase in the surface area thereof,

subjecting the resulting high sulfur coke to intimate contact with an excess of synthesis gas at a temperature in the range of about 275–430° F. and under an elevated pressure at which said metals are caused to catalytically react with carbon monoxide by the sulfur contained in said coke to form gasiform carbonyls of said metals,

separating the effluent synthesis gas containing metal carbonyls,

separating said carbonyls, and

thereafter subjecting said coke to hydrodesulfurization in the presence of synthesis gas at a temperature above approximately 1300° F.

2. The purification of a high sulfur petroleum coke as called for in claim **1** wherein at least a portion of the sensible heat of the synthesis gas effluent from the hydrodesulfurization step is employed to preheat the coke prior to preoxidation thereof and subsequently to effect metal carbonylation.

3. The purification of high sulfur petroleum coke as called for in claim **1**, wherein said carbonylation step is conducted at a pressure substantially above atmospheric in the range at which said metal carbonyls remains in gasiform phase.

4. The purification of high sulfur petroleum coke as called for in claim **1** wherein said carbonylation step is conducted at a pressure in the range of about 450–750 p.s.i.g.

5. The purification of high sulfur petroleum coke as called for in claim **1** wherein said hydrodesulfurization step is conducted in the presence of hydrogen formed by simultaneously gasifying said coke at a temperature of about 1300–2400° F. by contact with a mixture of molecular oxygen and steam.

6. The purification of high sulfur petroleum coke as called for in claim **1** wherein said hydrodesulfurization is conducted in the presence of a stream of synthesis gas at a temperature about 1300° F.

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EDWARD J. MEROS, Primary Examiner

U.S. Cl. X.R.

23—203; 201—17

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(5/69)

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,595,965 Dated August 24, 1971

Inventor(s) William F. Franz & Howard V. Hess

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the specification:
Col. 1, line 50 change "the" (second occasion) to --and--
Col. 3, line 47 change "500" to --450--
Col. 4, line 32 change "is" to --its--

Signed and sealed this 4th day of January 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Acting Commissioner of Patents