

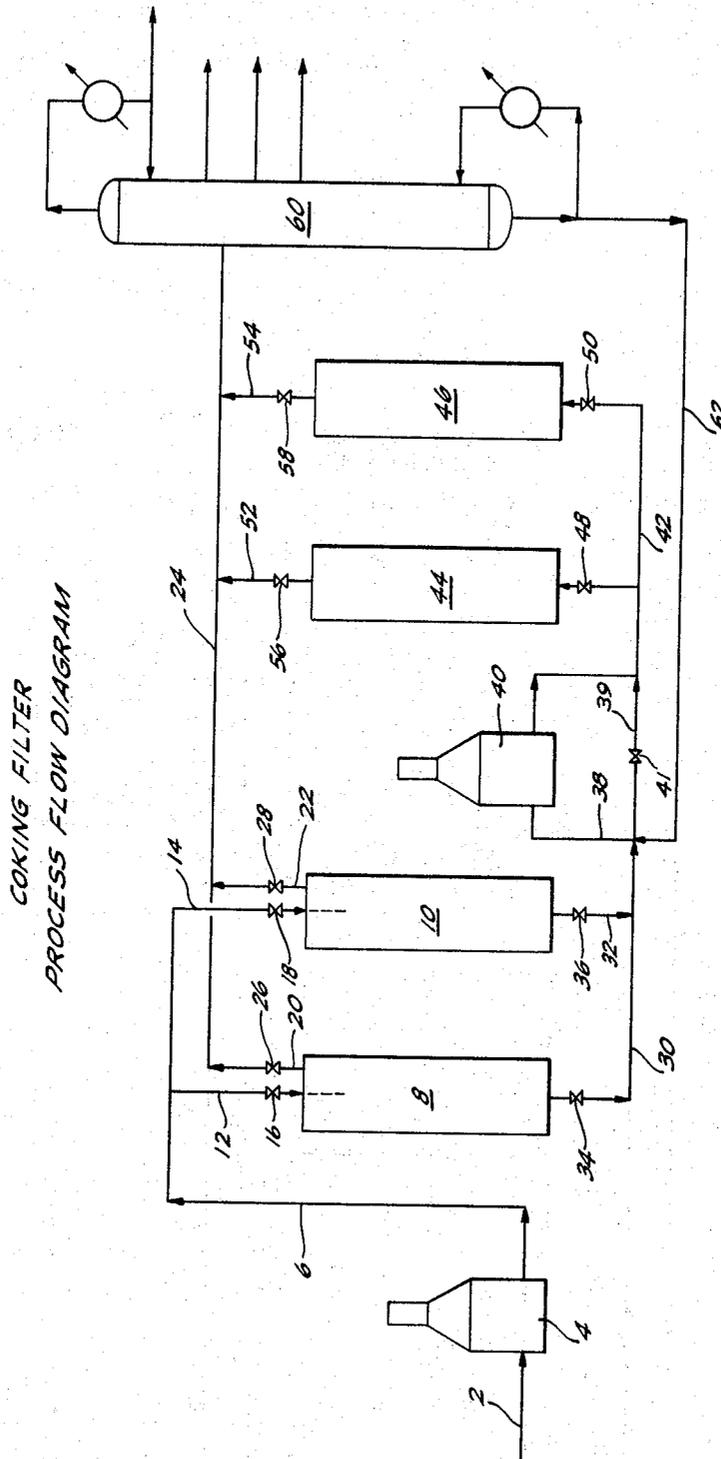
Oct. 30, 1973

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3,769,200

METHOD OF PRODUCING HIGH PURITY COKE BY DELAYED COKING

Filed Dec. 6, 1971



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1

3,769,200

METHOD OF PRODUCING HIGH PURITY COKE BY DELAYED COKING

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Filed Dec. 6, 1971, Ser. No. 205,132

Int. Cl. C10g 9/14

U.S. Cl. 208—53

13 Claims

ABSTRACT OF THE DISCLOSURE

A method for removing inorganic components from a coking feedstock is disclosed. In the method a feedstock containing inorganic impurities is passed through a first coking zone maintained at delayed coking conditions to reduce from 5 to 40 weight percent of the feedstock to coke and vapors. A liquid effluent is withdrawn from the first zone and passed through a second coking zone maintained at a temperature of 775° to 1000° F. and a pressure of 1 to 20 atmospheres absolute. The inorganic components are filtered from the feedstock by coke deposited in the first coking zone, thereby improving the purity of the coke produced in the second zone.

DESCRIPTION OF THE INVENTION

This invention relates to a method of removing inorganic matter from coking feedstocks and more particularly to a method of producing high quality coke from inorganic contaminated hydrocarbon feedstocks by delayed coking processes.

BACKGROUND OF THE INVENTION

In the production of coke by delayed cooking, a stream of high boiling hydrocarbons, typically reduced crude oil, is heated to thermal cracking temperatures and continuously introduced into a coking drum. The preheated hydrocarbons enter the bottom of the drum and are allowed to soak in their own heat for a period sufficient to convert the hydrocarbons to coke and vapors. The cracked vapors and vaporized hydrocarbons are continuously removed overhead of the coking drum and sent to a fractionating column while the coke is allowed to accumulate within the drum to successively higher levels. When the level of coke approaches the top of the drum the heated coking feedstock is diverted to another drum. The filled drum is then cooled and the coke removed therefrom, typically, by hydraulic jetstreams of water.

The quality of the product coke is greatly impaired when the feedstock contains large amounts of inorganic matter, typically metallic contaminants. These impurities are present in the feedstock as microparticulate suspensions and as oil-soluble organometallic compounds. The suspensions are filtered from the feedstock by the coke bed previously deposited within the coking drum. The oil-soluble metallic compounds are not vaporized and are either retained in the coke with the heavy hydrocarbon residue known as Volatile Combustible Material (VCM) or are cracked by the severe thermal coking conditions into vapor, coke and metal. In either event, the metallic portion is retained by the coke, thereby adding to the total contamination of the product coke.

Many industrial processes, which ultimately utilize the coke, such as the aluminum industry, cannot tolerate the presence of excess amounts of inorganic and particularly

2

metallic matter. Thus, when coke is produced from feedstocks having a high content of these impurities it is common practice to divert the product coke to industrial or commercial applications which can tolerate the impurities. Although several uses are available for the metal-contaminated coke, its employment in these applications certainly does not realize the remunerative gains associated with the premium grade coke.

Attempts to correct the metal content in the coke or to select feedstocks with a low impurity content have not heretofore been successful. Coke quality is generally of secondary significance in refining operations since the value of the distillates taken off overhead of the coking drums far exceeds the value of the coke. Accordingly, the refiners optimize the yield and quality of the distillates, often to the detriment of the coke products. Thus, selection of the most favorable feedstocks for premium coke production is not generally economically feasible.

More recently, however, coke is assuming a more important role in the process industries, and high quality cokes are commanding premium prices. Accordingly, a need exists for an improved coking process wherein contaminated feedstocks can be employed to produce premium cokes containing little if any inorganic matter.

It is therefore an object of this invention to provide a method for removing inorganic contaminants from hydrocarbon feedstocks and particularly coking feedstocks.

It is another object of this invention to provide a method of producing quality coke from coking feedstocks adulterated with inorganic matter.

It is an additional object of this invention to provide a method of producing high quality coke from the delayed coking of a feedstock containing large amounts of inorganic matter.

Other and related objects of this invention will become apparent to those skilled in the art from the following description of the invention and the attached drawings.

The aforementioned objects and attendant advantages can be realized by partially coking a feedstock in a first coking zone and using the coke deposited within the zone as a filter to remove the inorganic impurities. In the process the contaminated feedstock is passed through a first coking zone, hereinafter referred to as the filter zone, maintained at coking temperatures and pressures. The feedstock undergoes partial coking within the filter zone to effect a precipitation of the inorganic contaminants without reducing the entire feedstock to vapors and coke. A gas effluent comprising volatilized hydrocarbons and cracked vapors is continuously removed from the filter zone and sent to a fractionator to recover the gasolines, fuel oils, etc., components. An initial bed of coke is allowed to form within the zone, and a liquid effluent, comprising the uncracked and unvolatilized portion of the original feedstock, is withdrawn from the filter zone downstream from the coke bed. This liquid effluent contains substantially lesser amounts of the inorganic contaminant and can be thereafter completely reduced to high purity coke and vapors in a second coking zone maintained at delayed coking conditions.

The inorganic matter is substantially removed from the feedstock within the filter zone with little, if any, of the inorganic contaminant being retained by the withdrawn liquid effluent and carried over into the second coking zone. Thus, it is possible in the practice of this invention to recover a high purity coke from highly contaminated feed-

stocks. Although the coke produced in the first zone will be contaminated with a high content of inorganic material, it can be commercially utilized in processes capable of tolerating impurities. The high purity coke, on the other hand, can be recovered and sold at premium prices for use in processes demanding quality coke.

The rate at which the inorganic impurities are removed from the crude feedstock in the filter zone is dependent upon the coking severity and the size, i.e., cross-sectional area and volume, of the coke bed present within the zone. The coking severity controls the rate at which many of the organo-metallic compounds are reduced to vapors, coke and insoluble metallic precipitates, while the size of the coke bed determines the quality of the bed in removing by filtration or adsorption the inorganic microparticulate suspensions and metallic precipitates from the crude feedstock. For purposes of uniformity, the above-mentioned removal rate is hereinafter defined and referred to as the "filtration." I have found that as the coking severity within the filter zone increases, the filtration of inorganic matter from the feedstock similarly increases. Additionally, as the amount of coke progressively builds up to successively higher levels within the zone, the greater the filtration.

The desired filtration is dictated by the impurity content of the coking feedstock and also by the required purity of the product coke produced in the second zone. Where highly contaminated feedstocks are encountered, or where high purity cokes are desired, the filtration in the filter zone must be maintained at a relatively high level. I have found that from 50 to 700 weight parts of the inorganic impurities per million parts of crude feedstock can be removed by reducing approximately 5 to 40 weight percent of the feedstock to coke and vapors within the filter zone.

The essence of this invention can be more readily understood by reference to the attached drawing which displays a representative flow diagram of one specific embodiment of this invention. Referring now to the drawing, a coking feedstock containing an excess of inorganic impurities is introduced to preheater 4 through line 2. The feedstock is heated to coking temperatures within the heater and thereafter pumped through line 6 to parallel connected downflow filter drums 8 and 10. By connecting the filter drums in this manner, the process can be operated in a continuous manner by diverting the preheated feedstock to an empty filter drum while the other drum is shut down for decoking and cleaning. The alternative drum feeding is accomplished by lines 12 and 14 and sealed with valves 16 and 18 respectively. While the above parallel connection of two filter drums is illustrated, it is recognized that other embodiments can be employed which do not change the essence of the claimed invention. A brief discussion of other less preferred embodiments are presented infra.

The preheated feedstock is introduced into the top of drum 8 or 10 and is allowed to soak within the drum in its own heat to effectuate partial coking. While undergoing partial coking some of the lighter hydrocarbons in the feedstock are vaporized while other hydrocarbons present are thermally cracked to coke and vapors. The resulting gas effluent is withdrawn overhead through vapor recovery lines 20 and 22 and sent to a fractionator 60 through vapor line 24. Recovery lines 20 and 22 are similarly sealed with valves 26 and 28 so as to allow alternative feeding of filter drums and, accordingly, continuous processing.

The crude feedstock travels downwardly within the filter drum while undergoing partial coking and passes through a bed of previously deposited coke. When the partially cracked feedstock reaches the bottom of the filter drum the filtered feedstock, comprising the liquid effluent, is withdrawn by recovery lines 30 and 32. These lines are sealed to filter drums 8 and 10 with valves 34 and 36 respectively to accommodate continuous processing. Al-

though the filtered feedstock can be diverted to other uses, it is preferred to subject substantially all of the feedstock to further coking so as to reduce it to vapors and dry coke. Accordingly, filtered feedstock is introduced through lines 39 and 42 into the bottom of two parallel connected upflow coking drums, 44 and 46. By utilizing a parallel connection, the feedstock can be diverted into one drum while the alternate drum is undergoing decoking and cleaning. The two drums are sealed from line 42 by valves 48 and 50.

In a preferred embodiment, the filtered feedstock is preheated after its removal from the filter drum but prior to its introduction into the coking drums. In this embodiment, the filtered feedstock is introduced through line 38 into preheater 40. After the feedstock is heated to the desired temperature it is introduced through line 42 into the aforementioned upflow coking drum 44 or 46.

The preheated filtered feedstock is allowed to soak in its own heat within the coking drum to completely reduce the feedstock to coke and vapors. The vapors are taken off overhead through vapor lines 52 and 54 and sent to fractionator 60 through vapor recovery line 24. The vapor lines 52 and 54 are sealed with valves 56 and 58, respectively, so as to allow shutdown of one drum for decoking and cleaning while allowing delayed coking to take place in the other drum. The vapors entering fractionator 60 are separated into light gases, gasolines, lower boiling hydrocarbons and a heavy residuum. The residuum is collected and recirculated to the filtered feedstock stream at line 38 immediately before heater 40 for additional cracking and coke formation.

While the aforescribed flow process describes a preferred embodiment of this invention, numerous modifications can be made without changing the essence of the claimed invention. For instance, the filter zone (drums 8 and 10) does not have to be constructed of downflow coking drums and, accordingly, upflow drums can be utilized with the liquid effluent being drawn off the side of the drums or at the top by operating the drums in a flooded condition. In another embodiment, the heavy residuum from the fractionator may be recycled to the crude feedstock stream at line 2 so as to be subjected to a second filtration. In another embodiment, coke is allowed to accumulate to a desired height in a conventional coking drum and thereafter, the drum is converted into a filter by withdrawing a liquid effluent from the drum and sending it to a second coking drum. In another embodiment, the filter zone is maintained within the same drum as the coking zone so that only one delayed coking drum is necessary. In another embodiment, a contaminated feedstock may be subjected to filtration in accordance with this invention and the liquid effluent from the filter zone may be combined with a relatively contaminant-free feedstock and the combined mixture introduced into the coking zone. In another embodiment, the process is conducted in a batchwise manner. It is apparent that numerous obvious modifications can be made without changing the inventive concepts of this invention and such are considered within the practice of this invention as defined by the appended claims.

The filter process of this invention can be effectively utilized with any of the commonly employed coking feedstocks. Generally these feedstocks are high boiling hydrocarbon mixtures having at least 50 volume percent of hydrocarbons boiling above about 750° F. and preferably between 850° and 1200° F. Typical feedstocks include virgin crude, bottoms from atmospheric and vacuum distillation, thermal tar, Duo-Sol extract, furfural extract, vacuum tar, reduced crude, topped crude and blends thereof. High aromatic content feedstocks are also suitable for coking and exemplary feedstocks include refractory cycle stocks obtained from thermal and catalytic cracking processes and boiling in the gas-oil range; decant oil from fluid catalytic cracking; etc.

The above feedstocks commonly contain large amounts of inorganic impurities. Those inorganic contaminants most commonly encountered include vanadium, nickel, iron, silicon, copper, molybdenum, aluminum, cobalt, calcium, etc. Although the above impurities may be present in the coking feedstock, those impurities which are particularly burdensome in the process are the metallic compounds of vanadium, nickel, and iron, and more particularly vanadium. It is not known how all of the inorganic impurities enter the coking feedstock system or in what state they exist.

Many of the metallic components exist as organo-metallic compounds, e.g., porphyrins and high molecular weight carbonaceous coke precursors, such as, asphaltenes and resins. The porphyrins are the most commonly encountered and are complex cyclic proteins characterized by the cyclic connection of four pyrrole rings. The asphaltenes are generally characterized as being insoluble in n-pentane and have molecular weights which vary over a considerable range. Analysis of these constituents has illustrated that the molecular weight range is approximately delineated by the limits of 1000 to about 30,000 AMU's. The resin fraction is defined as that material which is soluble in n-pentane but insoluble in n-propane.

The major part of the vanadium, calcium, iron and nickel contaminants in the coking feedstock, is present in the original crude oil—generally as organo-metallic compounds. It is believed, however, that a small amount of the nickel and iron contaminants enters the coking feedstock from the corrosion of metallic vessels, lines, etc. The silicon, cobalt and molybdenum contaminants usually enter the feedstock stream from extraneous sources, such as catalyst degradation in the catalytic cracking processes, etc. The copper and aluminum contaminants also extraneously enter the feedstock stream by the corrosion of aluminum and copper-containing vessels and abrasion of the metal-containing bearings and seals in pumps, etc.

As indicated above, the type and amount of contaminant is, to a great extent, dictated by the source of the coking feedstock. For example, the coking of virgin crude oil, reduced and topped crude and bottoms from atmospheric and vacuum distillation of crude oil are generally contaminated with large amounts of vanadium, nickel and iron. Feedstocks from the Duo-Sol extract, furfural extract, decant oil and refractory cycle stocks from catalytic cracking processes are more or less contaminated with silicon, iron, nickel and aluminum with trace amounts of molybdenum and cobalt. When blends are employed, all of the inorganic contaminants may simultaneously be present.

The amount of inorganic contaminant varies considerably with the type of feedstock and origin of the crude oil. The following Table 1 presents the typical concentrations for the various components which are frequently encountered in coking feedstocks. The concentration of the inorganic impurity is presented in weight parts per million (p.p.m.) based on the weight of the unfiltered coking feedstock.

TABLE 1
Contaminant concentration in feedstock (p.p.m.)

Contaminant	Broad range	Usual range
Vanadium.....	20-500	50-300
Nickel.....	10-300	30-250
Iron.....	10-300	30-250
Silicon.....	3-250	5-100
Calcium.....	3-150	3-100
Copper.....	0-30	0-10
Molybdenum.....	0-15	0-10
Cobalt.....	0-15	0-10
Aluminum.....	3-100	3-50

The total amount of inorganic contaminants within typical feedstocks commonly ranges from 100 to 1500

parts per million and more commonly from 100 to 1000 parts per million.

Many industrial processes utilizing coke have set forth standards for the maximum inorganic content for the coke. The aluminum industry, for example, demands that the graphite employed in the electrolytic processing of aluminum must be made from coke having an inorganic content less than the amounts recited in the following Table 2 for the respective impurity.

TABLE 2
Maximum contaminant concentration (p.p.m.)¹

Contaminant	Maximum content	Acceptable range
Vanadium.....	250	0-200
Nickel.....	250	0-200
Silicon.....	300	0-250

¹ Weight parts per million based on the weight of coke.

Cokes having a contaminant concentration below the maximum allowable amount recited in the above Table 2 can be prepared from contaminated feedstocks such as disclosed in Table 1 supra. In practicing the instant invention, a preheated feedstock is introduced into the filter zone maintained at coking conditions. The feedstock is allowed to soak in its own heat to thermally crack some of the hydrocarbons to coke and vapors. The vapors and volatilized hydrocarbons are withdrawn from the filter zone and sent to a fractionator while coke is allowed to slowly accumulate within the zone. An initial layer of coke or primordial bed is allowed to form within the filter zone while no liquid effluent is being removed. When the coke level within the zone attains a depth of from 1 to 10 feet and preferably from 2 to 8 feet, the liquid effluent is then continuously withdrawn. While it is unnecessary to close the liquid effluent lines during the formation of the primordial bed, I have found that when the effluent is immediately withdrawn from the filter zone some contaminants are initially carried along with the effluent to the coking zone. Additionally, problems with liquid channelling through the coke bed are more frequently encountered when the primordial bed is not initially formed, thereby reducing the effectiveness of the bed in removing the microparticulate suspensions and metallic precipitates.

The filter zone is maintained at coking conditions sufficient to reduce from 5 to 20 weight percent, preferably from 5 to 15 weight percent, and most preferably from 7 to 13 weight percent of the incoming crude feedstock to dry coke within the zone. This reduction is commonly referred to as the coke yield. The desired coke yield within the filter zone can be controlled by manipulating the feedstock flow rate or its residence time within the filter zone and the coking severity, i.e. the temperature and pressure, within the zone. When mild coking conditions are employed to obtain the desired coke yield, the liquid effluent withdrawn from the zone must be preheated before its introduction into the second coking zone. Alternatively, where intermediate preheating is undesired, the coke yield is maintained within the desired range by utilizing high feedstock through-puts through the zone. These two alternatives are respectively discussed hereinafter.

WITHOUT INTERMEDIATE PREHEATING

In instances where the liquid effluent is withdrawn from the filter zone and introduced directly into the second coking zone, elevated coking temperatures and pressures must be maintained in the filter zone in order to obtain the desired coking severity in the second zone.

Generally, the average temperature within the filter zone must be maintained between about 800° and 1100° F. and preferably from 825° F. to 950° F. The gas pressure at the top of the zone is generally maintained at 1 to 35 atmospheres and preferably from 2 to 15 atmospheres absolute. The coke yield in the filter zone is suppressed and maintained within the desired limits by operating at high feedstock flow rates. I have found that the desired coke yield can be obtained by utilizing feedstock flow rates sufficient to maintain the residence time within the filter zone below 2 hours and preferably from 0.1 to 1 hour. The residence time for purposes herein is defined and determined by dividing the volume of the filter zone by the flow rate of the feedstock to the zone.

WITH INTERMEDIATE PREHEATING

In a preferred embodiment of this invention, the liquid effluent from the filter zone is preheated prior to its introduction into the coking zone. In this embodiment the desired coke yield in the filter zone can be obtained by operating at relatively mild coking conditions comprising average zone temperatures of 700° F. to 850° F. and preferably at 700° F. to 800° F. and pressures of 1 to 15 atmospheres absolute, and more preferably from 1 to 10 atmospheres absolute.

The coking conditions in the filter zone are preferably maintained more severe initially when low bed levels are encountered. Generally, these initial conditions are temperatures of from 775° F. to 850° F. and pressures of from 1 to 10 atmospheres absolute.

As the coke progressively builds up within the filter zone, it is preferred that the coking severity is progressively decreased. By operating the zone in this manner, the filtration of inorganic impurities can be maintained relatively constant throughout the filling of the zone. When the coke nears the top of the filter, or when the coke depth approaches 35 to 40 feet, very mild coking conditions are preferably maintained. Generally, these final coking conditions are from 600° to 740° F. and 1 to 20 atmospheres absolute, and preferably from 600° to 700° F. and 2 to 15 atmospheres absolute. I have found that the temperature of the feedstock within the filter zone can be decreased by 2½ to 3½ degrees Fahrenheit for each foot of coke produced in the filter drum.

The coking zone is maintained at conventional coking conditions in order to completely reduce the filtered feedstock to coke and vapors. Typical coking conditions are maintained at 800° to 875° F. and 2 to 10 atmospheres absolute.

The vapors from the coking zone are recovered overhead and subjected to fractionation. The bottoms from the fractionator are preferably preheated and returned to the coking drum for further coking. I have found that returning from 10 to 20 volume percent, and preferably from 11 to 15 volume percent, based on the volume of crude feedstock, of the bottoms from the fractionator results in the production of good coke while recovering a maximum amount of lighter gasolines and fuel oils. Although the vapors are preferably recovered overhead from the filter zone in a separate vapor stream, it may be advantageous in some instances to recover the vapors in the same recovery line as the liquid effluent stream.

The following examples are cited to illustrate the results obtainable in the practice of specific embodiments of this invention, but are not to be construed as limiting the scope of the invention as defined by the appended claims.

EXAMPLE 1

This example is presented to demonstrate the filtration of inorganic matter from a coking feedstock within a filter zone by the practice of the invention. A coking feedstock having the properties set forth in the following Table 3 is employed in this example,

TABLE 3

Coking feedstock properties

	Gravity (° API) -----	8.7
5	Initial boiling point (° F.) -----	579
	5 vol. percent (° F.) -----	681
	10 vol. percent (° F.) -----	726
	50 vol. percent (° F.) -----	969
	Maximum boiling point (° F.) -----	1177
10	Pour point (° F.) -----	60
	Sulfur content (wt. percent) -----	1.54
	Nitrogen (wt. percent) -----	1.07
	Viscosity (SS. at 210° F.) -----	644
	Carbon residue ¹ (wt. percent) -----	10.7
15	Pentane insoluble (wt. percent) -----	8.7

¹ Measured by the Conradson method.

The feedstock having the aforesaid properties is preheated to a temperature of 920° F. and then injected into the bottom of a filter drum. The drum is 13 feet in diameter and the filter zone within the drum is 10 feet in height. The preheated feedstock enters the bottom of the drum at a rate of approximately 19,000 barrels per day, thereby providing a residence time within the filter zone of approximately 25 minutes. At this flow rate, the filter zone is completely flooded with a liquid effluent being continuously withdrawn from the top of the zone and immediately introduced into a coking drum. The coking drum is 60 feet in height and has a diameter of 13 feet. The vapors and lighter hydrocarbons are taken overhead from both the coking and filter zones and sent to a fractionator. The bottoms of the fractionator are recycled to the preheater at a rate of approximately 13 volume percent of the original feedstock charge.

The coking conditions in the filter zone are maintained at an average temperature of about 850° F. and an average pressure of about 60 p.s.i.g. The coking conditions in the coking drum are maintained at an average temperature of about 830° F. and an average pressure of about 40 p.s.i.g. Approximately 7 weight percent of the fresh feedstock is converted to dry coke within the filter zone. The liquid effluent withdrawn from the filter zone is completely reduced to coke and vapors in the coking drum. When the coke builds up in the drum to a depth of 40 feet, the feedstock is diverted to another filter and drum. The hot coke is then cooled with steam.

Coke samples from the filter zone are removed and segregated for inorganic material content analysis. Similarly, coke samples from the top 10 feet in the coking drum are removed and segregated for later analysis.

The coke samples from each zone are analyzed by emission spectrography for vanadium, nickel, copper and iron content. The results from these analyses are presented in the following Table 4.

TABLE 4
Inorganic material content

Inorganic	Content (p.p.m.)		
	Filter zone	Second zone	Percent reduction
Vanadium.....	335	168	50
Nickel.....	270	185	31
Copper.....	21	4	81
Iron.....	170	93	45

As illustrated by the above Table 4, the inorganic material content in the coke dropped considerably from the filter zone to the coking zone. This decrease in content demonstrates the inorganic filtration discussed aforesaid.

EXAMPLE 2

This example is presented to illustrate the practice of this invention with a process which is exemplified by the flow diagram in the accompanying drawing. In the process, a first preheater is connected to two vertical

downflow filter drums (corresponding to drums 8 and 10 in the drawing) arranged in parallel. The bottom of each filter drum is connected to a second preheater with the outlet from this preheater connected to three vertical upflow coking drums. The coking drums are connected in parallel with a common overhead vapor line connecting each drum to a fractionator. The bottoms of the fractionator are recycled to the second preheater.

The filter drums are each 40 feet in height and 12 feet in diameter. The coking drums are each 60 feet in height and 13 feet in diameter.

A coking feedstock having the properties and containing several contaminants at concentrations set forth in Table 5 is heated in the first preheater and charged into the top of one of the downflow filter drums. The feedstock enters the drum at a rate of approximately 21,000 barrels per day. The coking conditions are varied during the coking procedure so that the filtration is held relatively constant during the filtering process. During start-up, no liquid effluent is withdrawn from the filter drum for a period of approximately 1 hour and sufficient to form a primordial coke bed of about 1-3 feet of coke. After the hour period, a liquid effluent corresponding to approximately 18,000 barrels per day is withdrawn from the bottom of the filter zone. At this time, the average drum temperature is approximately 825° F. The temperature is gradually decreased with an increasing amount of coke in the filter drum at the rate of 3° F. for each foot of coke within the drum. Thus, when the coke attains a depth of 30 feet within the drum, the filter drum is maintained at a temperature of 735° F. The drum pressure is maintained at a pressure of about 55 p.s.i.g. throughout the filtering process.

The filtered coking feedstock is withdrawn from the bottom of the filter drum and heated to a temperature of 930° F. within the second preheater. The preheated feedstock is then introduced into the bottom of one of the coking drums and allowed to soak therein in its own heat during the coking period. The drum pressure is maintained at 30 p.s.i.g. and the average drum temperature is approximately 840° F. When the coke builds up to a depth of 40 feet in the coking drum, the filtered feedstock is diverted to another drum. The hot coke is then cooled with steam and thereafter removed.

The vapors and lighter hydrocarbons from both the filter and coking drums are then drawn off overhead and sent to a fractionator. The bottoms from the fractionator are recycled to the second preheater at a rate of approximately 10 volume percent of the original feedstock charge.

The coke from the coking drums are analyzed for vanadium, copper, silicon, iron, and nickel content by emission spectrography. The coke is found to be within the acceptable ranges as set forth in the specification.

TABLE 5

Coking feedstock properties

Gravity, ° API -----	9
Initial boiling point (° F.) -----	570
Maximum boiling point (° F.) -----	1200
Sulfur content (wt. percent) -----	1.8
Nitrogen content (wt. percent) -----	1.0
Viscosity (SS. at 210° F.) -----	645
Carbon residue ¹ (wt. percent) -----	12
Pentane insolubles (wt. percent) -----	8.7
Inorganic content (p.p.m.):	
Vanadium -----	150
Nickel -----	90
Iron -----	10
Silicon -----	50
Copper -----	3

¹ Measured by the Conradson method.

I claim:

1. A method of removing inorganic components from a cokable hydrocarbon mixture having at least 50 volume percent of the hydrocarbons boiling above about 750° F. and containing in excess of 100 weight parts per million of said inorganic components which comprises:

passing said hydrocarbon mixture into a filter drum containing a bed of coke having a depth of at least 1-10 feet at delayed coking conditions sufficient to reduce from 5 to 50 weight percent of the hydrocarbon mixture to coke and vapors;

withdrawing said vapors from the filter drum; withdrawing a liquid hydrocarbon effluent from said filter drum through said coke bed and downstream thereof; and

coking said liquid effluent in a second coking drum maintained at delayed coking conditions sufficient to reduce said liquid effluent to coke and vapors.

2. The method defined in claim 1 wherein said inorganic components are selected from vanadium, nickel, iron, silicon, calcium, copper, molybdenum, cobalt, aluminum or mixtures thereof.

3. A method of producing high purity coke from a coking feedstock containing from 100 to 1500 weight parts per million of inorganic components which comprises:

coking a portion of said feedstock in a first coking drum at delayed coking conditions in an amount sufficient to deposit a coke bed at least one foot to ten feet in depth in said drum;

passing the remainder of said feedstock through the first coking drum and said coke bed at delayed coking conditions sufficient to reduce from 5 to 40 weight percent of said feedstock to coke and vapors;

withdrawing the vapors from said first coking drum during said coking;

withdrawing a liquid hydrocarbon effluent from said first coking drum through said coke bed and downstream thereof; and

coking said liquid effluent in a second coking drum maintained at delayed coking conditions sufficient to reduce said liquid effluent to coke and vapors.

4. The method defined in claim 3 wherein the coking conditions in said first coking zone are maintained at temperatures of 800° to 1100° F. and pressures of 1 to 35 atmospheres absolute and wherein said feedstock is passed through said first coking zone at a rate sufficient to realize a residence time therein of 0.1 to 2 hours.

5. The method defined in claim 3 wherein the coking conditions in said second coking zone are maintained at temperatures of 780° to 875° F. and pressures of 2 to 10 atmospheres absolute.

6. The method defined in claim 3 wherein said inorganic components include microparticulate suspensions of said components in said feedstock.

7. The method defined in claim 3 wherein said inorganic components are selected from vanadium, nickel, iron, silicon, calcium, copper, molybdenum, cobalt, aluminum or mixtures thereof.

8. The method defined in claim 7 wherein said inorganic components include vanadium, nickel, iron or mixtures thereof and are present as organo-metallic compounds soluble in said feedstock.

9. The method defined in claim 3 wherein said liquid effluent is preheated prior to its introduction into said second coking drum sufficient to maintain the temperature in the second drum higher than in said first drum.

10. A method of producing a coke containing less than 200 weight parts per million of metallic components from a coking feedstock containing from 100 to 1500 weight parts of vanadium, iron, nickel or mixtures thereof per million parts of said feedstock which comprises:

coking a portion of said feedstock in a first coking zone maintained at a temperature of 700° to 850° F. and a pressure of 1 to 15 atmospheres absolute and in an

11

amount sufficient to deposit a coke bed at least one foot to ten feet depth in said first zone;
 passing the remainder of said feedstock through the first coking zone and said coke bed at the said temperatures and pressures and sufficient to reduce from 5 to 40 weight percent of said feedstock to coke and vapors with a coke yield of from 5 to 20 weight percent;
 withdrawing the vapors from said first coking zone during said coking;
 withdrawing a liquid hydrocarbon effluent from said first coking zone through said coke bed and downstream thereof;
 preheating said liquid effluent; and
 coking said preheated liquid effluent in a second coking zone maintained at delayed coking conditions more severe than said first coking zone and comprising a temperature of about 780° to 875° F. and a pressure of about 2 to 10 atmospheres absolute sufficient to reduce said liquid effluent to coke and vapors.

11. The method defined in claim 10 wherein the temperature in said first coking zone is initially from 775° to

12

850° F. and decreased at a rate of from 2 to 3 degrees for each foot of coke deposited in said first zone.

12. The method defined in claim 10 wherein said first coking zone is a downflow coking drum and said second coking zone is an upflow coking drum.

13. The method defined in claim 10 wherein said vapors are taken overhead from said first and second coking zones and subjected to fractionation and wherein the bottoms from the fractionation represents from about 10 to 18 volume percent of said coking feedstock and is recycled to said coking zone.

References Cited

UNITED STATES PATENTS

15	2,775,549	12/1956	Shea	208—52
	2,813,824	11/1957	Gorin	208—53
	3,472,761	10/1969	Cameron	208—131
	2,334,306	11/1943	Barron	208—52

20 HERBERT LEVINE, Primary Examiner

U.S. Cl. X.R.

208—131