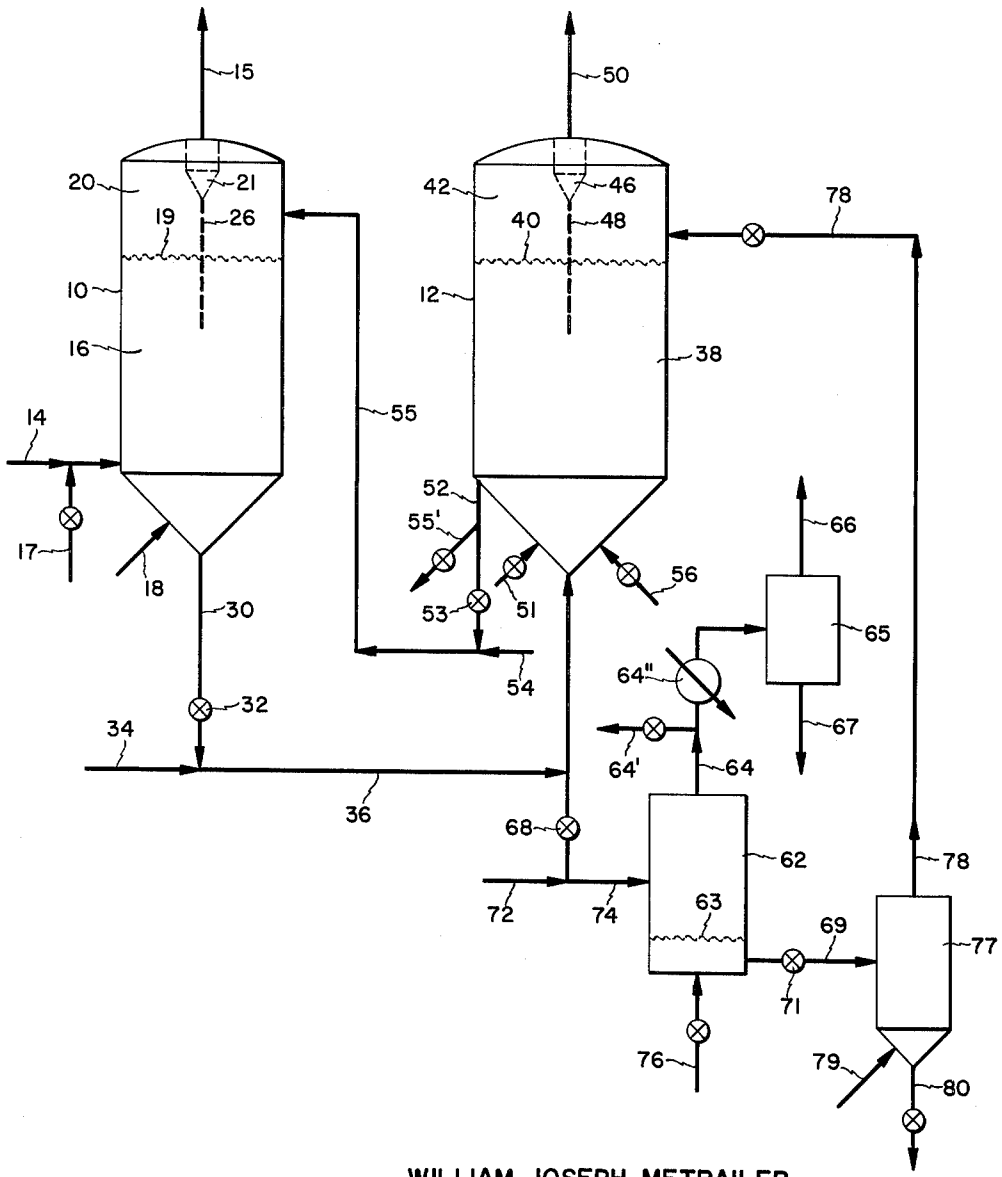
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COKING OF HYDROCARBONS WITH THE REMOVAL OF METALLIC CONTAMINANTS FROM THE COKE

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WILLIAM JOSEPH METRAILER
JOHN FREDERICK MOSER, JR. Inventors

By Gary J. Gilbert

Patent Attorney

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COKING OF HYDROCARBONS WITH THE REMOVAL OF METALLIC CONTAMINANTS FROM THE COKE

William Joseph Metrailer and John Frederick Moser, Jr., Baton Rouge, La., assignors to Esso Research and Engineering Company, a corporation of Delaware

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This invention relates to coking of heavy petroleum residual oils to produce lower boiling hydrocarbons and coke having a low metals content.

Many residual petroleum oils contain large amounts of metals such as vanadium, nickel, iron, etc. which deposit on the coke formed when carrying out a fluid coking process in a dense turbulent fluidized bed. If the coke particles are to be used in the manufacture of carbon anodes or electrodes for use in the aluminum industry, the metals content and especially the vanadium content of the coke particles should be low to avoid contamination of the aluminum product.

Various processes are known in the prior art for removing certain metals from coke by halogen treatment but these processes are ineffectual for the removal of vanadium or other contaminating metals from fluid coke. These prior art processes were suggested for use in demetallizing coke made from coal or the like or from petroleum coke from the delayed coking process.

Fluid coke from the fluid coking process is a different type of petroleum coke, that is, it is made by a different process and has different characteristics. The fluid coking process is a well known commercial process having been described in articles and being disclosed in Pfeiffer et al. Patent No. 2,881,130 granted Apr. 7, 1959 and other patents. In this process fluid coke particles are circulated between the reactor where the heavy residual oil is thermally cracked and coked and the burner where the coke particles are reheated by burning part of the coke product. The reheated coke particles are then recycled to the reactor. Thus, the coke particles after having a layer of coke deposited on them in the reactor are then heated to a higher temperature in the burner which results in partial devolatilization and baking of the freshly deposited coke. This cycle is repeated many times to form spherical coke particles having layers of coke in an onion-like formation or layer-on-layer formation or a shell within a shell structure.

Even though there is burning of some or a part of the coke particles, the coke particles in the coking reactor grow in size during the process due to the fact that there is a net deposition of coke. In this deposition of coke there are also deposited the contaminating metals such as vanadium in the layer-on-layer formation. Each fluid coke particle has a new layer of coke added as it passes through the coking reactor and increases in size. The coke particle then passes through the burner vessel where it is heated and at least some of the volatile hydrocarbon material is released. This happens as each coke particle with its new and additional layer of coke is passed through the burner vessel to release some of the volatile material during heating. However, the contaminating metals are not volatilized in the burner vessel.

By having this coke particle circulation from lower to high temperature zones, each succeeding layer of coke is baked on the nucleus and the resulting coke particles are much stronger and denser than coke obtained in other types of commerical coking processes. In addition, as each layer of coke is deposited, the metals such as vanadium are entrapped and covered over by superposed layers of coke which protest the deposited metals and make

removal of such metals from the interior of the fluid coke particles virtually impossible. Some of the surface metals can be removed from the exterior of the coke particles by known processes but this is not sufficient to remove the metals content to a desirable low number. This action is diffusion limited and the halogen gas does not penetrate far enough to remove any substantial amount of metals.

According to the present invention a fluid coking process is practiced in such a manner as to reduce the metals content, such as vanadium, of fluid coke particles by substantially continuously treating the fluid coke particles with a mixture of a halogen such as chlorine and an oxygen-containing gas such as air or air enriched with oxygen to convert the metals in the coke layers being formed to volatile halogen compounds such as a volatile chloride or oxychloride or the like. This treatment is preferably integrated with the coker burner so that by this substantially continuous treatment, each successive layer of coke is substantially demetallized as it is formed thereby overcoming the problem of diffusion of the treating gas through the shell-like structure of the coke particles which arises if treatment is deferred until the coke particle has reached its final product size.

The air and chlorine are introduced into the burner vessel as a mixture or as individual streams while the burner vessel is being operated to burn or partially oxidize the fresh layer of coke on the coke particles. Or a separate treating vessel can be installed in addition to the burner vessel to treat part or all of the coke stream circulating between the coker vessel and burner vessel. The air or other oxygen-containing gas heats the coke particles and the halogen gas forms volatile metal compounds which pass overhead with the flue gas.

In a broader form of the invention coke is treated at an elevated temperature with a mixture of oxygen-containing gas such as air and a halogen such as chlorine or halogen compounds such as hydrogen chloride, carbon tetrachloride etc. which would decompose to form free halogen under conditions specified, to remove contaminating metals such as vanadium. During the treatment with the mixed oxygen-containing gas and halogen there is some reduction of sulfur in the coke product.

The vanadium-containing vapors released during the treatment with the mixed treating gases can be recovered, if desired, and in this operation it may be desirable to operate in a separate vessel with a high concentration of halogen and to add a limited amount of air or oxygen as such. Where the volatile metal compounds are to be recovered, countercurrent flow of coke particles to be treated and the mixture of treating gases may also be desirable.

In the drawing the figure represents diagrammatically one form of apparatus adapted to carry out the process of the present invention.

Referring now to the drawing, the reference character 10 designates a coking vessel and reference character 12 designates a burner vessel. Liquid hydrocarbon feed is introduced or sprayed into coking vessel 10 through line 14. Liquid feeds suitable for the present invention are heavy or reduced crude petroleum oils or vacuum bottoms or residual hydrocarbon oil which cannot be vaporized without decomposition. Such oil feeds may have an API gravity between about −10° and 20°, and a Conradson carbon between about 5 and 50 weight percent. The oil feed can be preheated by conventional means, not shown, or by exchange with the reactor vapor products discharged from line 15 to between about 400 to 800° F. and is introduced into the dense fluidized turbulent coke bed 16 in the coking vessel 10. Preferably the oil feed is introduced into the fluidized bed 16 at a multiplicity of points. The highly turbulent nature of the fluid-

ized bed 16 also assists in causing rapid dispersion of the oil feed throughout the bed 16.

The oil feed is usually a residual oil containing metal contaminants such as vanadium, nickel, iron, etc., which are deposited on the coke formed during coking and form impurities in the coke. The present invention is concerned with removal of these impurities. The amount of vanadium present in the residual oil feed may be between about 50 and 1000 p.p.m. (parts per million) and the amount of nickel in the residual oil feed may be between about 50 and 1000 p.p.m.

Preferably the oil feed is injected into the bed 16 in a highly dispersed state. About 0.25 and 5.0 weight percent steam on the oil feed may be used to assist in dispersing the oil feed in the bed 16. The steam is preferably introduced through line 17 into a dispersing nozzle (not shown). The coking vessel 10 contains coke particles ranging in size between about 40 and 5000 microns with most of the particles being between about 75 and 2500 microns. Steam is also introduced through line 18 into the bottom portion of the fluid bed of coke 16 to function as a stripping gas to remove or displace hydrocarbon vapors from the coke. Stripping gas velocity is between about 0.3 and 5.0 ft./sec. The stripping gas may be injected into the dense fluid coke bed through nozzles at high velocity to cause attrition or grinding of the larger coke particles to maintain the desired coke particle size. To be effective as an attrition gas, the steam is introduced at supersonic velocities.

The coke particles within the bed 16 are maintained in a turbulent dense fluidized condition by the gases and vapors passing upwardly therethrough. The gases and vapors include the fluidizing and stripping gas and the vapors and gases formed by coking or cracking of the oil feed. The fluidized bed 16 has a level indicated at 19 superimposed by a dilute phase 20. The average superficial velocity of the upflowing gaseous material is between about 0.5 and 5.0 ft./sec. depending on the size of the coke particles making up the bed 16. The density of the fluid bed 16 may be between 30 and 70 lbs./cu. ft. The temperature in the bed 16 and vessel 10 is maintained between about 850° and 1200° F. Higher temperatures up to about 1800° F. or higher may be used in processes for cracking the oil feed to olefins, diolefins, aromatics, etc., and coke.

The pressure in coking vessel 10 may be between about 1 and 150 p.s.i.g. The hydrocarbon oil feed rate may be between about 0.1 to 5.0 weight of oil per hour per weight of solids (W/Hr./W) present in the fluid bed 16. In the fluid bed 16, the oil feed is cracked or converted to hydrocarbon vapors and coke. The vaporous hydrocarbons are lower boiling hydrocarbons and these hydrocarbons leaving the bed 16 and passing into the dilute phase 20 carry entrained solids. In the dilute phase 20, there is some settling of solids.

The vapors and gases passing up through dilute phase 20 are passed into gas-solids separating means 21 such as one or more cyclone separators in series arranged inside and at the top of coking vessel 10 for separating entrained solids from vapors and gases which pass out overhead through line 15. The separated solids are returned to or above the dense fluidized bed 16 through dip leg 26.

The vapors and gases passing overhead through line 15 are further treated as desired and may be fractionated to separate gasoline from higher boiling hydrocarbons and gas and the higher boiling hydrocarbons may be recycled to the coking vessel or removed from the system as product. They may also be used to preheat the oil feed to the reactor.

To supply heat for the coking vessel 10, coke particles are circulated from vessel 10 to burner vessel 12 where partial combustion of the coke particles occurs and the coke particles are heated to a higher temperature. Coke particles are withdrawn from the bottom portion of the

coking vessel 10 through standpipe 30 having a control valve 32 at its lower end and suspended in a fluidizing gas which may be air, steam or the like introduced through line 34 below valve 32 and the resulting suspension is passed through line 36 into the lower portion of burner vessel 12. The burner vessel is preferably a two phase burner where the coking particles settle out to form a dense fluidized turbulent bed 38 having a level indicated at 40 superimposed by a dilute phase 42. In the burner vessel 12, a portion of the coke is consumed by burning with air and the remainder of the coke particles are heated to a temperature between about 50° F. and 300° F. higher than the temperature in coking vessel 10, that is, between about 1050° F. and 1250° F. Other types of burners such as a high velocity transfer line burner or the like may be used instead of the fluid bed burner.

The combustion gas passes up into dilute phase 42 and there is some separation and settling of the entrained coke solids. The combustion gas then passes into gas solids separation means 46 such as one or more cyclone separating means located inside and at the top of burner vessel 12 to separate entrained solids which are returned to the dense fluidized bed 38 through dip leg 48. Hot combustion gas passes overhead through line 50 and may be passed through a waste heat boiler (not shown) or other heat exchanger means to recover heat from the combustion gas before venting it to the atmosphere. Air is introduced into the bottom portion of burner vessel 12 through line 51.

The gases passing up through burner vessel 12 maintain the coke particles in a dense turbulent fluidized condition. The gases pass up through the bed 38 at an average superficial velocity between about 0.5 and 5.0 ft./sec. and the density of the fluid bed 38 is between about 30 and 70 lbs./cu. ft. The hot coke particles are withdrawn from dense fluidized bed 38 in burner vessel 12 through standpipe 52 having a control valve 53 and steam or the like is introduced below the valve 53 through line 54 and the suspension passed through line 55 and recycled to the upper portion of coking vessel 10. Coke may be removed from standpipe 52 through line 55' as product, if desired.

As pointed out above the contaminating metal such as vanadium or nickel is deposited in successive layers and the metal is extremely difficult to remove from the final coke product. With the present process the coke particles are subjected to the action of a mixture of treating gas containing oxygen, such as air, and a halogen-containing compound or gas such as chlorine in the burner vessel while the coke particles are being reheated before being recycled to the reactor vessel. In this way after fresh coke is deposited on the coke particles in the coker vessel, the coke particles are passed to the burner vessel where this fresh deposit or layer of coke is subjected to the action of air and chlorine at the burner vessel temperature and contaminating metals or at least a portion thereof is removed and passed overhead from the burner vessel as a volatile metal compound or compounds. Chlorine is added either through line 51 or 56.

The amount of air intoduced into burner vessel 12 through line 34 and line 51 and passing to the burner vessel 12 is about 0.05 to 1.0 pounds per pound of coke entering the burner vessel 12 by way of line 36 to raise the temperature of the coke particles between about 50° F. and 300° F. higher than the temperature in the coking vessel 10, that is, between about 1050° F. and 1250° F. The amount of chlorine added to the air either through line 51 with the air or through a separate line 56 may be between about 1 and 150 mols of chlorine per mol of vanadium on the coke entering the burner vessel 12 through line 36. This amount of chlorine may be varied further depending on the percent of the coke burned to supply the heat since the vanadium removal is related to the amount of the coke oxidized in the process.

The volatile metal chlorides and/or metal oxychlorides leave the burer vessel 12 through line 50 along with the products of combustion.

Instead of treating the coke particles in the burner vessel 1 with the mixture of air and chlorine, the treatment with the gas treating mixture can be done in a separate vessel 62 communicating with reactor vessel 10 via lines 30, 36 and 74. Such a vessel is shown in the drawing at 62 containing a fluidized dense solid bed of coke particles therein shown at 63. The coke particles which are withdrawn from reactor vessel 10 flow into standpipe 30 extending downwardly from the reactor 10 and through line 36 to a point where line 36 joins line 74. Line 74 is provided with control valve 68 which permits a portion of the coke to pass into vessel 62 and the rest pass to burner 12. Gas, such as air, inert or the like, is introduced through line 72 into the withdrawn coke particles below valve 68 to form a dilute suspension which is passed through line 74 into the vertically arranged vessel 62. Or the vessels may be arranged at proper elevations so that the coke flows by gravity through line 74 and the control valve 68 and be introduced as a dense fluidized stream without introduction of a suspending gas through line 72. When using a separate vessel 62 the amount of chlorine (Cl_2) used may be between about 1 and 300 mols of chlorine (Cl_2) per mol of vanadium in the coke introduced into vessel 62.

Treating gas including air and chlorine is introduced into the bottom portion of treating vessel 62 through valve line 76 for upward passage therethrough. The treating and any other gas passing up through the treating vessel 62 is selected in an amount to produce a superficial velocity in vessel 62 between about 0.1 and 3.0 feet/sec. The vapors containing combustion gases, the volatile metal chlorides and/or metal oxychlorides leave vessel 62 overhead through line 64. The gases may be discarded through line 64′ or they may be cooled in cooler 64″ and passed into vessel 65 to recover the metallic chlorides and/or metallic oxychlorides through bottom withdrawal line 67. In operations where the metallic chlorides and/or metallic oxychlorides are recovered, part of the off gases may be recycled from line 66 back to the treating vessel 62 through line 76.

The coke flows from vessel 62 through line 69 into vessel 77 which serves as an elutriator. The coke flow rate into the elutriator vessel 77 is regulated by control valve 71. Steam, inert or other gases are injected into vessel 77 along with some water through line 79 to quench the produce coke which is withdrawn through line 80. The velocity in vessel 77 is maintained between 5.0 and 10.0 feet per second so that a major portion of the coke smaller than about 300 microns is carried back to the burner vessel 12 through line 78.

The conditions of temperature and treatment with the mixed treating gas may be substantially the same in vessel 62 as described previously for burner vessel 12. However, as subsequent data will show, metals removal can be accomplished over a wide range of conditions when combinations of oxygen-containing gas and chlorine are employed. Since vessel 62 is thermally independent of the rest of the fluid coking system, it may be operated over a temperature range of about 650° F. to 1250° F. or higher. Also, when recovery of the metal chlorides and/or metal oxychlorides is desired, the quantity of oxygen introduced through line 76 may be limited to that required to give sufficient oxidization of the coke to permit vanadium removal.

Or part of the treatment with air and chlorine may be done in burner 12 and part in separate vessel 62.

The flue gas passing overhead through line 50 from burner vessel 12 contains vanadium and metallic halogen or oxyhalide vaporous compounds and excess halogen and/or halide gas. This flue gas may be passed through a waste heat boiler or a cooler or condenser (not shown) to condense or precipitate out the vanadium and other volatile metallic compounds.

The present invention is especially adapted for substantially continuous treatment of coke to remove metal contaminants as they are laid down in the fluid coking process. The substantially spherical coke particles produced in the fluid coking process are known to have a shell within a shell structure. This structure is formed by successive or superimposed layers of carbon or coke which are laid down on the coke particles as they are passed from the burner vessel 12 to the coker vessel 10 where a layer of coke is deposited, and then back to the burner vessel 12 where the fresh layer of coke is partially oxidized to supply the heat required for the coking process. By the substantially continuous treatment of the coke particles with a mixture of air and chlorine, each successive layer of coke is demetalized soon after it is formed and this overcomes the problem of diffusion of the treating gas through the shell-like structure which arises if the treatment for vanadium removal is deferred until the coke particle has reached its final product size.

The data in Table I show that best vanadium removal is obtained by simultaneous treatment with air and chlorine. The data also show that the simultaneous treatment with air and chlorine can be effected under conditions existing in a normal fluid coking process. The data also show the unexpected result that substantial amounts of vanadium can be removed using a mixture of air and chlorine at the very low temperature of about 650° F.

Table I

Run No.	Treating Conditions			Coke feed	Coke Product		Percent Vanadium Removed	
	Gases Used	Temp., ° F.	Time, Hrs.	P.P.M. Vanadium	Wt. Percent	P.P.M. Vanadium	From Coke	Based on Vanadium In
1	98% N_2+2% Cl_2	1,100	2	500	97	465	7	10
2	98% N_2+2% Cl_2[1]	1,100	2	500	71	655	[2] Increase	7
3	Cl_2[1]	1,800	2	500	81	575	[2] Increase	7
4	98% Air+2% Cl_2	1,100	2	500	91	425	15	23
5	88% Air+12% Cl_2	1,100	2	500	83	305	39	49
6	88% Air+12% Cl_2	650	10	500	90	440	12	21
7	88% Air+12% Cl_2	750	7	500	80	320	36	49
8	91% Air+9% Cl_2	1,100	2	630	83	415	34	45

[1] After air oxidation at 700° F. with air+11% H_2O to increase the surface area of the coke to about 194 M^2/gm.
[2] Because oxidation in absence of Cl_2 increases concentration of coke and Cl_2 alone does not give much vanadium removal.

In Table I the percentages of gases used are given by volume and the treatment was carried out by placing fluid coke particles in a vessel and then passing the gas or gas mixtures through the fluid coke particles. The vessel was provided with auxiliary heating or cooling as needed to maintain the temperature at the desired level.

The data in Table I were obtained in a single pass treatment and they show that the use of inert gas plus chlorine is not as good as air plus chlorine and that separate

treatment with oxygen first to increase the surface area of the coke particles shows the ineffectiveness of treatment with chlorine in the absence of oxygen at the conditions normally existing in a fluid coke burner vessel. Due to the fact that the separate treatment with oxygen consumes coke or carbon but not the metal contaminants, the actual vanadium content of the coke particles from the separate treatments was higher than in the original coke feed.

Coke consumption in the burner vessel under normal conditions is between about 10 and 40 weight percent of the total coke made in the reactor. The data in Table I show that the consumption or burning of coke per pass is well within that necessary to supply heat to the coking process and by doing this substantially continuously in a multipass treatment with chlorine addition in the burner vessel the final coke particle product will contain small amounts of vanadium.

With the present invention it is only necessary to add chlorine to the burner vessel or to the air going to the burner vessel and since part of the coke is normally consumed to supply heat to the fluid coking process, the attendant coke consumption in the present process is minor.

The data in Table I clearly show that treatment of fluid coke particles with a mixture of air and chlorine (Run 4) gives two to three times as much vanadium removal as treatment with chlorine and nitrogen at identical operating conditions (Runs 1 and 2) or treatment with chlorine alone at more severe conditions (Run 3). In Run 4, about 130 mol Cl_2 was introduced per mol of vanadium in the coke charged in the bed. The data also show that vanadium removal can be obtained over a wide range of operating conditions when mixtures of air and chlorine are used. The data also show that vanadium content of the coke product decreases as the coke yield decreases with a wide range of operating conditions and that this indicates that vanadium removal is diffusion limited. The time of treating the coke particles with the air-chlorine mixture in the burner vessel 12 may be between about 10 minutes and 4 hours. The time of treating the coke particles with the air-chlorine mixture in a separate treating zone such as vessel 62 may be between about 30 minutes and 10 hours. The tempearture during treatment with air and chlorine may be between about 600° F. and 1300° F.

Under the conditions of treatment of the present process it is believed that the vanadium probably leaves as a vanadyl chloride including VOCl, $VOCl_2$ or $VOCl_3$ as these compounds are slightly more volatile than equivalent vanadium chlorides but the invention is not to be restricted to removal as vanadyl chlorides. The present invention teaches how to remove vanadium from coke and is not to be limited as to the actual vanadium compound or compounds removed.

In a specific example feeding about 3400 barrels per day of residual petroleum oil containing about 115 p.p.m. of vanadium and having a gravity of about 5.3° API, an initial atmospheric boiling point of about 835° F., and a Conradson carbon of about 25 weight percent are introduced into coking vessel 10 along with about 12 weight percent of steam on the fresh oil feed. The density of the fluid coke bed 16 in coker vessel 10 is about 45 lbs./cu. ft. and the temperature of the coking fluid bed 16 in coker vessel 10 is about 980° F. The pressure in vessel 10 is high enough to overcome the pressure drop through the recovery system and is slightly above atmospheric pressure. Vaporous cracked products pass overhead through line 15 and are cooled, condensed and fractionated to separate lower boiling hydrocarbons and gases as follows together with the coke formed:

Gas, C_3 minus (lbs./day)	140,000
C_4 (B/day)	150
C_5–430° F. (B/D)	650
430–1015° F. (B/D)	1,550
Coke, gross (tons/day)	170
Coke, particle size range (microns)	40–5000

About 40 tons of the coke per day are burned in burner vessel 12 to supply the heat required for the coking step in vessel 10. The temperature in the burner vessel is about 1140° F. The circulation rate of the coke solids between the coking vessel 10 and burner vessel 12 is about 4.5 tons per minute.

Without any treatment to remove vanadium, the coke product will contain about 500 p.p.m. of vanadium. To reduce the vanadium in the coke poduct obtained when practicing the present invention to about 200 p.p.m. or less, about 6 mols of chlorine per mol of vanadium in the coke entering the burner vessel 12 are introduced into the vessel 12 through line 56 during the coking process. This will amount to about 0.003 pound of chlorine per pound of coke being introduced through line 36 into the burner vessel 12. The amount of air introduced into the burner vessel 12 through line 51 is about 0.1 pounds per pound of coke being introduced through line 36 into burner vessel 12. In this specific example about 0.0024 pounds of chlorine per pound of air is introduced into burner vessel 12.

The coke particles in passing back and forth between the coker vessel 10 and burner vessel 12 are treated each time they are in the burner vessel. The coke particles individually circulate between the coker vessel 10 and burner vessel 12 between about 10 and 60 times before they are withdrawn as product.

The coke particles withdrawn as product from the present process through line 55' will contain about 100 p.p.m. of vanadium.

The present invention can be easily adapted to fluid coking units as it is only necessary to inject or introduce chlorine or other suitable halogen or halogen compound into the fluid coker burner vessel so that the fluid coke particles are treated with a mixture of oxygen, an oxygen-containing gas or air and chlorine or halogen or halogen containing compound in the burner vessel.

The temperature for treating coke with mixed air and chlorine to remove vanadium may be as low as 600° F. As shown in Table I there was appreciable removal of vanadium at a temperature of 650° F. maintained for about 10 hours. The temperature may be between about 600 and 1300° F. preferably between about 600° F. and 800° F. in order to reduce the corrosive rate of halogen compounds on material normally used in construction. When operating in this manner, the auxiliary treating vessel 62 may be employed. When an auxiliary treating system is employed only about 10 to 50% of the circulating coke stream is diverted into the auxiliary treating vessel and the number of times the coke is treated is thereby reduced to between about 5 and 20 times before it is withdrawn as product coke. It was noted that during vanadium removal there was some sulfur reduction in the coke product, the sulfur probably going off as $SOCl_2$ or a similar halide.

What is claimed is:

1. A method of removing metal contaminant from coke which comprises simultaneously treating the coke with a gas containing free oxygen and a halogen-containing material at a temperature of at least about 600° F.

2. A method of removing vanadium from petroleum coke which comprises burning a portion of the coke to heat the coke to at least 600° F. while contacting it with a halogen-containing material.

3. A method according to claim 2 wherein said halogen-containing material comprises chlorine.

4. In a method of coking heavy petroleum oils to produce coke and lower boiling hydrocarbons wherein the oil is cracked in a fluid coking reaction zone and the fluid coke particles are partially burned with air in a burner zone and returned to said coking reaction zone to supply the heat of cracking and a portion of the fluid coke particles is removed as product, the improvement which comprises substantially continuously introducing chlorine gas and air into said burner zone to substantially continuously

remove contaminating metal from the fluid coke particles while partially burning the coke particles.

5. In a method of coking heavy petroleum oils to produce coke containing metal impurities and lower boiling hydrocarbons wherein the oil is cracked in a coking reaction zone and coke particles are partially burned in a burner zone and recycled to said coking reaction zone to supply the heat of cracking, the improvement which comprises withdrawing a portion of the coke particles from said reactor zone and passing them to a separate confined treating zone, introducing a halogen-containing material and a gas containing free oxygen into said separate confined treating zone to burn at least a portion of the coke particles in the presence of halogen-containing material and to form volatile metal halide compounds and recovering, as a product, coke particles with a reduced metal impurity content.

6. A method for removing vanadium from petroleum coke particles which comprises treating said coke particles at a temperature between about 600° F. and 1300° F. by contacting them with a gas containing free oxygen and chlorine.

7. A method according to claim 6 wherein the amount of chlorine introduced in said step comprises between about 1 and 150 mols of chlorine per mol of vanadium in the coke particles introduced in said treating step and a portion of the coke particles is burned to heat the coke particles to a temperature in said range.

8. A method of removing contaminating metal from petroleum coke particles which comprises contacting said coke particles at a temperature between about 600° F. and 1300° F. with a gas containing free oxygen and a halogen-containing material.

9. A method according to claim 8 wherein said contaminating metal comprises vanadium, the coke comprises fluid coke, the gas containing free oxygen comprises air and the halogen-containing material comprises chlorine.

10. A method according to claim 5 wherein gas containing volatile metal halide compounds formed in said treating zone and combustion gases are passed overhead from said treating zone and cooled to condense and recover the metal halide compounds formed in said treating zone.

11. A method according to claim 6 wherein the oxygen containing gas comprises air.

12. A method according to claim 11 wherein the off gases from said treating step are cooled to condense and recover a volatile vanadium compound formed during the treating step.

13. A method according to claim 1 wherein the coke comprises fluid coke particles and the gas containing oxygen comprises air.

14. A method according to claim 1 wherein the coke is treated with a mixture of air and chlorine.

15. A method according to claim 1 wherein the time of treatment is between about 10 minutes and 10 hours.

16. A method according to claim 6 wherein the amount of chlorine introduced in said step comprises between about 1 and 300 mols of chlorine per mol of vanadium in the coke particles introduced in said treating step.

17. A method according to claim 1 wherein the contaminating metal comprises vanadium, the halogen-containing material comprises chlorine, the gas containing free oxygen is air and between about 1 and 150 mols of chlorine per mol of vanadium in the coke particles are introduced in said treating step along with 0.05 to 1 pound of air per pound of coke treated in said treating step.

18. A method according to claim 9 wherein sufficient air is used to burn part of the coke particles and heat them to a temperature above about 600° F., the amount of chlorine used is between about 1 and 150 mols per mol of vanadium in the coke particles and the time of treating is between about 10 minutes and 10 hours.

19. A method of coking heavy petroleum oils to produce coke containing metal impurities and lower boiling hydrocarbons, which comprises cracking a heavy petroleum oil in a fluid bed in a coking reaction zone, withdrawing coke particles and passing them to a fluid bed in a burner zone, continuously introducing air and a gaseous halide into said burner zone to burn part of said coke particles and to remove metal impurity by reaction with said halide each time the coke particles pass through said burner zone, removing some of said coke particles as product and recycling the rest of said coke particles to said coking reaction zone to supply the heat of cracking.

20. A method according to claim 19 wherein the metal impurity comprises vanadium, the temperature in said coking reaction zone is between about 850° F. and 1200° F., the temperature in said burner zone is between about 1050° F. and 1250° F., the volatile halide comprises chlorine, the amount of chlorine introduced into said burner zone comprises between about 1 and 150 mols of chlorine per mol of vanadium in said coke particles and the amount of air introduced into said burner zone comprises about 0.05 to 1 pound per pound of coke treated in said treating step.

21. In a process for coking a heavy petroleum oil containing metal impurities by contacting the heavy petroleum oil coking charge stock at a coking temperature with a body of coke particles maintained in the form of a dense turbulent fluidized bed in a coking zone wherein the oil is converted to product vapors and carbonaceous solids containing contaminating metal are continuously deposited on the coke particles, removing product vapors from said coking zone, removing coke particles as product, heating the circulating coke particles removed from the coking zone in a separate burning zone to burn part of the coke particles and to increase the temperature of the coke particles, returning the circulating heated coke particles from the heating zone to the coking zone to supply heat thereto, and wherein the fluid coke product particles normally contain metal impurities, the improvement which comprises continuously contacting the hot circulating coke particles in said burning zone with a gaseous halogen material at a temperature in the range of 600° F. to 1300° F. whereby contaminating metal is continuously removed from the circulating coke particles and their metals content lowered.

22. A process for coking a heavy petroleum oil containing metal impurities including vanadium which comprises contacting the heavy petroleum oil coking charge stock at a coking temperature with a body of coke particles maintained in the form of a dense turbulent fluidized bed in a coking zone wherein the oil is converted to product vapors and carbonaceous solids including contaminating metal are continuously deposited on the coke particles, removing product vapors from said coking zone, burning circulating coke particles removed from said coking zone in a burning zone to increase the particle temperature, contacting the circulating coke particles in said burning zone while in the form of a dense turbulent fluidized bed in said burning zone with a gaseous halogen containing material at a temperature in the range of 600° F. to 1300° F. to continuously remove contaminating metal therefrom while burning part of the coke particles, withdrawing a portion of the treated coke as product and recirculating the remainder to said coking zone.

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DELBERT E. GANTZ, *Primary Examiner.*

ALPHONSO D. SULLIVAN, *Examiner.*