

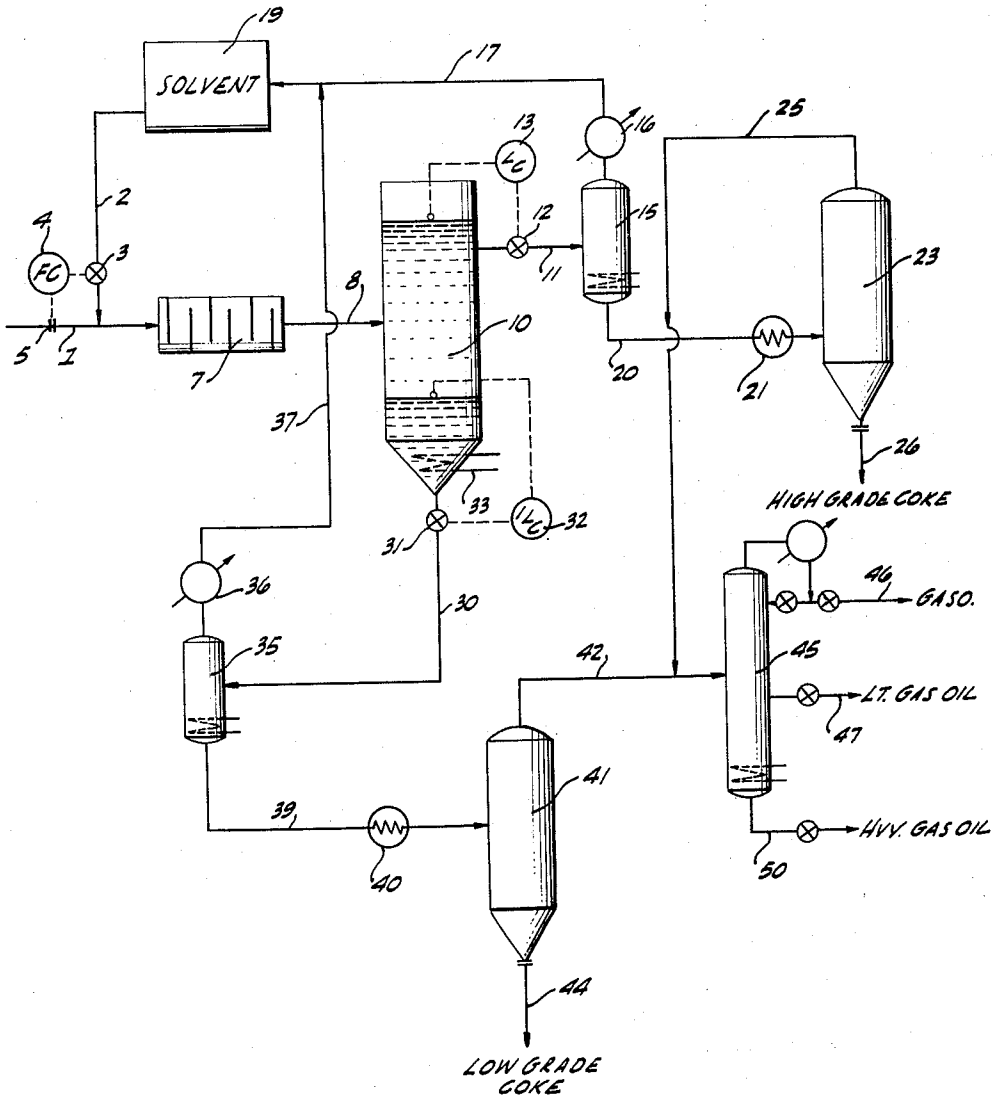
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COKING PROCESS

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COKING PROCESS

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This invention relates to thermal coking processes for converting low-quality crude oils and/or high-boiling residual oils into coke and lighter boiling fractions. Briefly, the invention resides in first subjecting the oil to solvent fractionation by adding thereto controlled amounts of C-4 to C-10 paraffinic hydrocarbons, then subjecting the paraffin-soluble portion to thermal coking to produce a high-quality coke, and separately coking the paraffin-insoluble portion to produce a low-quality coke. The principal advantage in the solvent-fractionation procedure is realized in the improved purity and low-ash value of the coke which may be formed from the paraffin-soluble portion of the feed. It has been discovered that the most deleterious contaminants in the feed, i.e. vanadium, nickel, and iron, are relatively insoluble in the paraffinic extract. Consequently the coke which is formed from the paraffin-soluble portion is relatively free of these metallic contaminants.

The initial solvent extraction, or solvent fractionation, step is broadly similar to conventional deasphalting procedures employing light paraffins to precipitate the asphaltic and more highly aromatic portions of the feed. However, as heretofore practiced, the use of light, normally gaseous paraffins is precluded herein because the extract represents too small a portion of the original feed, and coking of such extracts can produce only a small amount of coke, representing about 15-40% of the total coke available from the initial feed. Moreover, these conventional extracts are of sufficiently high quality (above 20° gravity API) for use as catalytic cracking stock, and it would hence be economically impractical to subject them to coking. By employing the higher paraffins, the extract will comprise from about 60% to 90% of the original feed, the insoluble raffinate constituting the remaining 10% to 40%. This extract is normally too low in gravity (below 20° API) for use as catalytic cracking stock, and coking thereof results in the production of about 40% to 75% of the total amount of coke which could have been produced by coking the initial feedstock. For purposes of the present invention it is hence preferred to control the extraction to produce an extract of below about 20° API gravity for coking.

A principal object of the present invention is to provide coking methods whereby crude oils which are contaminated with objectionable minerals such as vanadium and nickel may be treated so as to produce at least two different fractions of coke, in one of which the mineral contaminants are concentrated, and the other of which is relatively free of such contaminants.

Another objective is to provide methods whereby petroleum coke of sufficient purity for use as anodes in the production of aluminum by electrolysis may be produced from low-quality crude oils which normally produce coke which is too impure for such use.

Another object is to provide specific solvent extraction methods and specific solvents, which will effect the fractionation of coking feedstocks into two cokable fractions,

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each capable of producing substantially amounts of coke, and one of which produces a substantially higher quality coke than the other.

These objectives, as well as others which will appear hereinafter, are achieved by the process of this invention.

Thermal coking is a well-known and widely practiced operation in present day refining. It is generally employed to reduce the carbon content of low-quality reduced crude oils, distillation residues, and sometimes cracking residues. The process generally involves heating the oil to a cracking temperature of, e.g. 750°-950° F., and then transferring the heated oil to a coking drum where it is allowed to "soak" in its own heat for several minutes or hours while continuously removing overhead the volatile products boiling in the gas oil range and below, and continuously precipitating coke on the walls of the vessel. Ordinarily, none of the liquid feed is removed as liquid, all of the feed being converted either to coke, light gases, light distillates, or gas oil. The vaporized products are then segregated and put to their conventional uses.

Eventually, the coke which precipitates in the coke drum will fill the vessel, and at this point the operation must be suspended while the coke is removed. As the coke precipitates it adheres to the walls, and becomes strongly agglomerated into a dense, hard mass. This mass of coke is ordinarily removed either by drilling out the coke drum, or by washing it out with high-pressure jets of water.

It is known in the art that extraction of petroleum residues with liquid propane and/or butane is capable of producing a relatively high-gravity extract (20° to 40° API) which may be suitable for catalytic cracking stock. The original feed may have had a gravity of 4° to 15° API, and would thus be unsuitable for catalytic cracking because of the large amount of coke which would be formed on the catalyst. More generally however, such feeds are upgraded by coking instead of solvent extraction. Coking produces a high-gravity gas oil suitable for catalytic cracking, plus some gasoline, and by thermal decomposition most of the heavy aromatic portion is converted to coke.

In the present case, the objective is not to supplant coking by solvent extraction, but to use solvent extraction as an adjunct to coking in order to improve the coke quality. For this purpose it is preferred to use higher paraffinic solvents, for example, pentane, hexane, heptane, octane, nonane, decane, etc., or mixtures thereof. Light paraffinic gasoline fractions, or alkylate fractions, may also be employed. Straight-chain or branch-chain paraffins may be used, but the more highly branched hydrocarbons appear to be more efficient in rejecting the metallic contaminants, and are hence preferred. It is also contemplated to employ mixtures comprising a major proportion of any of the above paraffinic constituents, plus minor amounts of the lower paraffins, i.e. propane, butane, isobutane, etc. Butane or isobutane may be used alone if the temperature and proportions are carefully controlled so as to yield an extract oil of below about 20° API gravity. The use of mixtures of for example heptane, or alkylate, plus minor amounts of propane or butane, permits a reduction in the total volume of solvent employed, due mainly to the effect of the light paraffins in reducing the viscosity of the mixture, thereby promoting phase separation. Normally, about one to twelve volumes of solvent are employed per volume of oil. The higher paraffins are used in larger quantities, while the lower members are employed in the lesser proportions. In using decane for example, one would normally use about five to twelve volumes thereof per volume of feed. However, by admixing

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therewith about 5% to 20% of propane or butane, the combined solvent may be employed in proportions ranging between about three volumes to seven volumes per volume of oil. Pentane, hexane or heptane are normally used in proportions ranging between 4 and 10 parts per volume of oil.

Preferably the extraction is carried out at normal atmospheric temperatures. However, any temperature between about 0° and 200° C. may be employed, dependent in part upon the viscosity of the oil, and the boiling point of the solvent. Higher temperatures will normally result in dissolving a relatively larger amount of the feed, and concomitantly, of the metallic contaminants. The metal content of the extract oil is normally a function of the relative volume of extract oil and raffinate; the larger the volume of extract oil, the higher will be its metal content. The relative amount of extract oil produced should hence be controlled in accordance with the metal content of the feed, and the desired degree of purification.

The reject phase (raffinate) which separates upon extraction is initially a viscous slurry containing dispersed solvent and extract oil, and upon standing coalesces into a coke-like material which is solid at room temperature. For convenience it is hence preferable to utilize the initial liquid slurry, but if solidification occurs, the material may be heated to e.g. 100° to 300° C. to maintain it in liquid phase.

The process may perhaps be best understood with reference to the accompanying drawing which is a semi-diagrammatic flow sheet illustrating one modification. The invention is not however limited to the details of this illustration.

The initial feedstock is brought in through line 1 and admixed therein with solvent from line 2. The proper solvent ratio is maintained by the opening and closing of motor valve 3, controlled by flow controller 4 in response to the feed flow rate in line 1 through an orifice plate 5. The mixture of oil and solvent is then passed through a suitable mixing vessel as, for example, a baffle plate chamber 7, from which the mixture then passes through line 8 to settling chamber 10.

In settling chamber 10 the solvent-rich phase forms a supernatant layer which may be continuously withdrawn via line 11 by the operation of motor valve 12, responsive to liquid-level controller 13. The liquid extract in line 11 then passes into a flash chamber, or distillation column 15, from which solvent is removed overhead via condenser 16, and transferred via line 17 to storage chamber 19. The residue in column 15 constitutes the solvent-free extract oil, which is withdrawn through line 20 and preheated to coking temperatures in heater 21. Heater 21 is preferably a direct fired tube still through which the oil passes at a high flow rate so as to prevent the formation of coke in the heater. The preheated oil at a temperature of about 800° to 950° F., or preferably 850° to 900° F., is then admitted to delayed thermal coker 23, wherein coking is conducted without further addition of heat. Volatile products comprising gasoline and gas oil are continuously taken overhead via line 25, while fresh feed is continuously admitted via line 26 to maintain a substantially constant volume in coker 23. This operation is continued until the liquid mass in the coker becomes extremely viscous and eventually congeals and hardens into a porous coke mass adhering to the walls of the vessel. When this occurs the flow of feed is transferred to another coker unit, not shown, while coke is removed from vessel 23, as by drilling or hydraulic decoking. The high-grade coke thus produced is recovered via line 26. The overhead products from coker 23 are treated by distillation as hereinafter described.

The heavy lower phase which forms in separator 10 comprises the solvent-insoluble raffinate, which is continuously withdrawn via line 30 by the operation of motor

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valve 31 controlled by interface-level controller 32. As indicated above, it may be desirable to preheat this raffinate in order to maintain it as a pumpable liquid. This may be accomplished for example by means of steam coil 33 in the bottom portion of separator 10. The raffinate oil normally contains small amounts of solvent and extract oil, and is hence transferred via line 30 to a flash chamber, or small distillation column 35, from which solvent is taken overhead via condenser 36, and returned via line 37 to solvent storage 19.

The bottoms from column 35 are withdrawn via line 39, preheated in heater 40, which may be of similar design to heater 21. The preheated raffinate, at e.g. 850° to 900° F., is then passed into delayed thermal coker 41, wherein coking is continued in the same manner as described for coker 23, the volatile products being taken overhead via line 42. In some cases it will be found that the raffinate material is so viscous as to be difficult to preheat without undue coking in the heater coils. If this occurs, the viscosity may be reduced by recycling a portion of the overhead products from line 42 or line 25 to line 39.

When the material in coker 41 becomes substantially solidified, the flow of feed is preferably diverted to another coker not shown, while coker 41 is decoked in the same manner as described for coker 23. The relatively low-grade coke is removed through line 44.

The overhead products from cokers 23 and 41 may be treated in any desired manner for separation of the various products. In the case illustrated both streams are combined and subjected to fractional distillation in column 45. Coker gasoline is removed overhead via line 46, a side-cut light gas oil via line 47, and heavy gas oil bottoms via line 50. In some cases the overhead from coker 41 will differ substantially from that of coker 23, in which case it may be desirable to fractionate each overhead product separately. The overhead products from coker 41 are usually more aromatic in character than those from coker 23.

To illustrate further the effect of solvent extraction in producing high-quality cokes, the following examples are cited, which should not however be construed as limiting in scope:

Example I

A series of solvent extraction-coking experiments was carried out using as feed a Santa Maria Valley (California) residual oil containing a small proportion of high-boiling coker distillate recycle. The feed had the following characteristics:

Boiling range	_____° F.	Above 710
Gravity	_____° API	6.9
Sulfur	_____wt. percent	6.0
Vanadium	_____do	0.023
Nickel	_____do	0.014
Ash	_____do	0.13
Viscosity, SSF at 210° F.	_____	77.5

This feed, on direct coking at 880° F. yields 20.5% by weight of coke containing 5.1% sulfur, 0.11% vanadium, 0.055% nickel, and 0.36% total ash.

(A) *Propane extraction*.—A portion of the oil was extracted with 10 volumes of liquid propane. About 57% by weight of the oil was dissolved, leaving 43% of heavy raffinate oil. The solvent was then removed, and each fraction separately coked at 850° F. to give a combined coke yield of 19.9%. The extract oil produced about 12.3% by weight of coke, containing 0.15% ash, 0.004% vanadium and 0.007% nickel. The raffinate produced about 30% by weight of coke, containing about 0.17% vanadium. This example shows that coking of the propane extract produces a very high quality coke, but the amount produced is only 35% of the total. Moreover, the extract is sufficiently high quality to serve as catalytic cracking charge stock.

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(B) *Pentane extraction*.—Another portion of the feed was extracted with 10 volumes of pentane (90% n-pentane, 10% isopentane). About 78.5 wt. percent of the feed was dissolved, leaving 21.5 parts of solid raffinate. Upon coking the extract oil, 13.6% by weight of coke was produced, containing 0.05% vanadium, 0.03% nickel, and 0.23% ash. The raffinate produced about 47% of coke heavily contaminated with vanadium. The combined coke yield was 21.4%. Thus, by pentane extraction a coke was produced containing less than half as much vanadium as the coke from the original feed, and the extract produced 50% of the total coke.

(C) *Heptane extraction*.—Another portion of the feed was extracted with 10 volumes of heptane, resulting in solution of 83 wt. percent of the feed, leaving 17% of undissolved material. Coking of the individual fractions produced from the extract, 13.3 wt. percent of coke containing 0.06% vanadium, 0.035% nickel and 0.21% ash; and from the raffinate 50% of coke containing 0.19% of vanadium. The combined coke yield was 19.5%. Thus, by heptane extraction, 56% of the total coke produced is available from the extract, and such coke contains only about half as much vanadium as the coke from the total feed, and one-third as much as the coke produced from the raffinate fraction.

(D) *Alkylate extraction*.—Another portion of the feed oil was extracted with 10 volumes of depentanized alkylate (B.P. 200–300° F.) containing principally isohexanes, isoheptanes, and isooctanes. About 85 wt. percent of the oil was dissolved, leaving 15% of heavy raffinate, which was a granular solid at room temperature. The solvent-free extract oil was then subjected to coking, and 12.2 wt. percent of coke was produced containing 0.05% vanadium, 0.03% nickel and 0.21% ash. The raffinate produced 55% of coke which was heavily contaminated with vanadium. The combined coke yield was 18.65%. Thus, by alkylate extraction, 56% of the total coke produced is available from the extract, and such coke contains less than half as much vanadium as the coke from the total feed, and is suitable for use in manufacturing electrodes.

Example II

A slightly different feedstock consisting of a pure Santa Maria Valley residual oil was also subjected to heptane extraction followed by coking. The feed had the following characteristics:

Boiling range	°F.	Above 670
Gravity	°API.	5.8
Sulfur	wt. percent	6.7
Vanadium	do.	0.032
Nickel	do.	0.019
Ash	do.	0.12
Viscosity, SSF at 210° F.		99.7

This feed produces on direct coking at 850° F., 33 wt. percent of coke containing 0.105% vanadium, 0.046% nickel, and 0.36% total ash.

On extraction with 10 volumes of heptane, 75.8 wt. percent of the oil is dissolved, leaving 24.2% of heavy raffinate. On coking the extracted oil, 22.6 wt. percent of coke was produced containing 0.049% vanadium, 0.026% nickel and 0.18% ash. Thus, heptane extraction of this feed, followed by coking of the extract, produces 52% of the available coke, and the coke produced contains only about half as much vanadium and nickel as does the coke produced from the whole feed.

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When other feeds, other solvents, and other proportions thereof, are used in the above examples in accordance with the general disclosure herein, the same general results are obtained, i.e. a large proportion of the total available coke is produced from the extract, and said coke is substantially purer than that produced from the original oil. Hence, the invention is not limited to the details of the examples, and all variations which would occur to those skilled in the art leading to the same results, are included. The true scope of the invention is intended to be embraced by the following claims.

I claim:

1. A method for producing high-grade, low-ash coke of low vanadium content from a heavy mineral oil containing substantial amounts of metallic contaminants including vanadium, which comprises subjecting said oil to solvent extraction with a depentanized alkylate gasoline fraction boiling between about 200° and 300° F., said gasoline fraction containing principally isohexanes, isoheptanes, and isooctanes, thereby forming an extract phase comprising the major proportion of said oil, and a heavy raffinate phase constituting a minor portion of said oil, separating said phases, removing the solvent from said extract phase and subjecting the extract oil to thermal coking at a temperature between about 800° and 950° F., and recovering the high-grade coke so produced.

2. A process as defined in claim 1 wherein said solvent extraction is controlled so as to provide an extract oil having an API gravity of below about 20°.

3. A method for producing a high-grade coke containing less than about 0.06% vanadium from a heavy mineral oil containing at least about 0.01% vanadium, which comprises subjecting said oil to solvent extraction with a depentanized alkylate gasoline fraction boiling between about 200° and 300° F., said gasoline fraction containing principally isohexanes, isoheptanes, and isooctanes, thereby forming an extract phase comprising the major proportion of said oil, and a heavy raffinate phase constituting a minor portion of said oil, separating said phases, removing the solvent from said extract phase and subjecting the extract oil to thermal cooking at a temperature between about 800° and 950° F., and recovering the high-grade coke so produced.

4. A process as defined in claim 3 wherein said solvent extraction is controlled so as to provide an extract oil having an API gravity of below about 20°.

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