April 30, 1968 N. J. PATERSON 3,380,912

COMBINATION EXTRACTION-DEMETALATION PROCESS FOR HEAVY OILS

Filed March 1, 1967 2 Sheets-Sheet 1

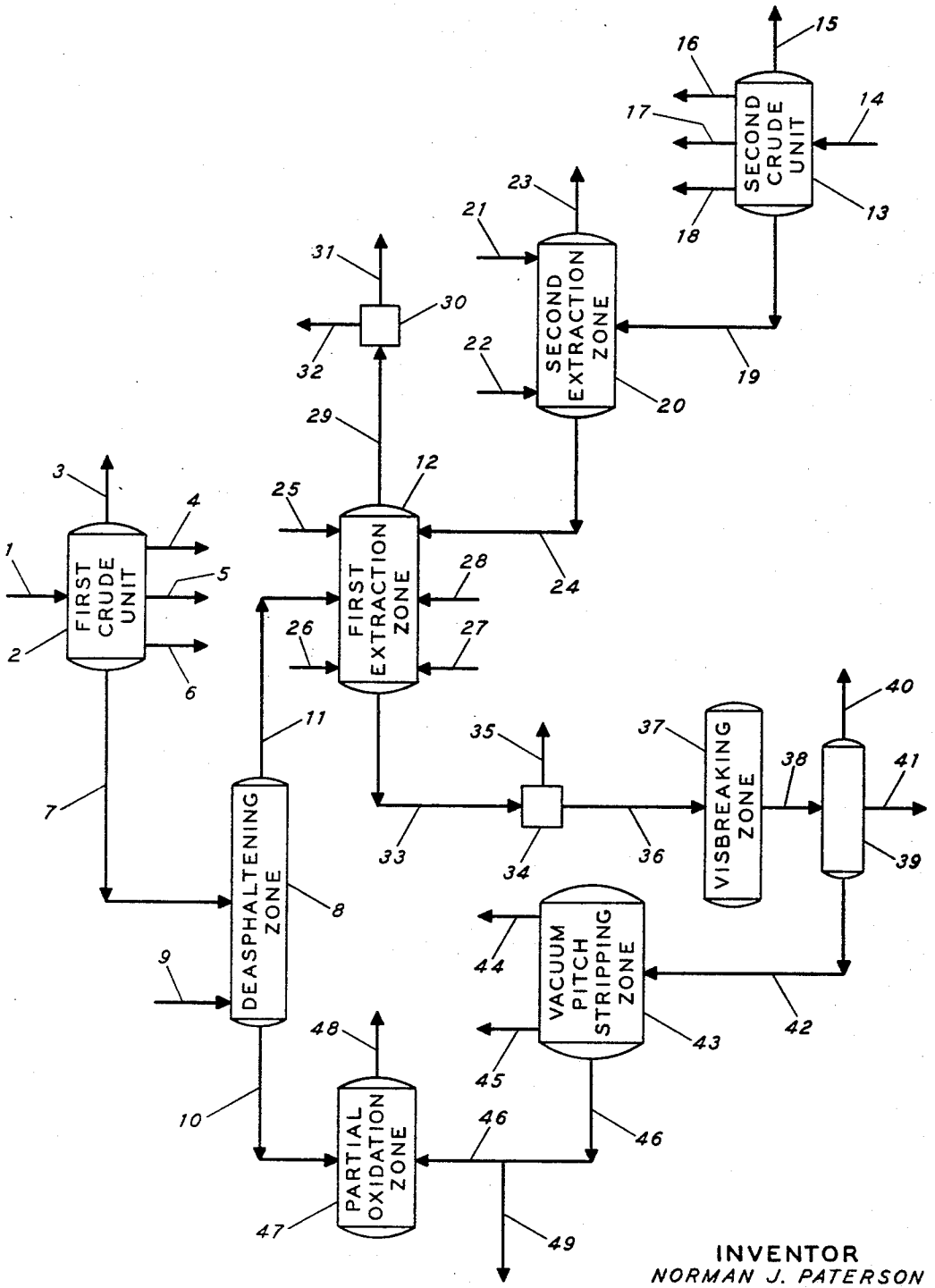

FIG. 1

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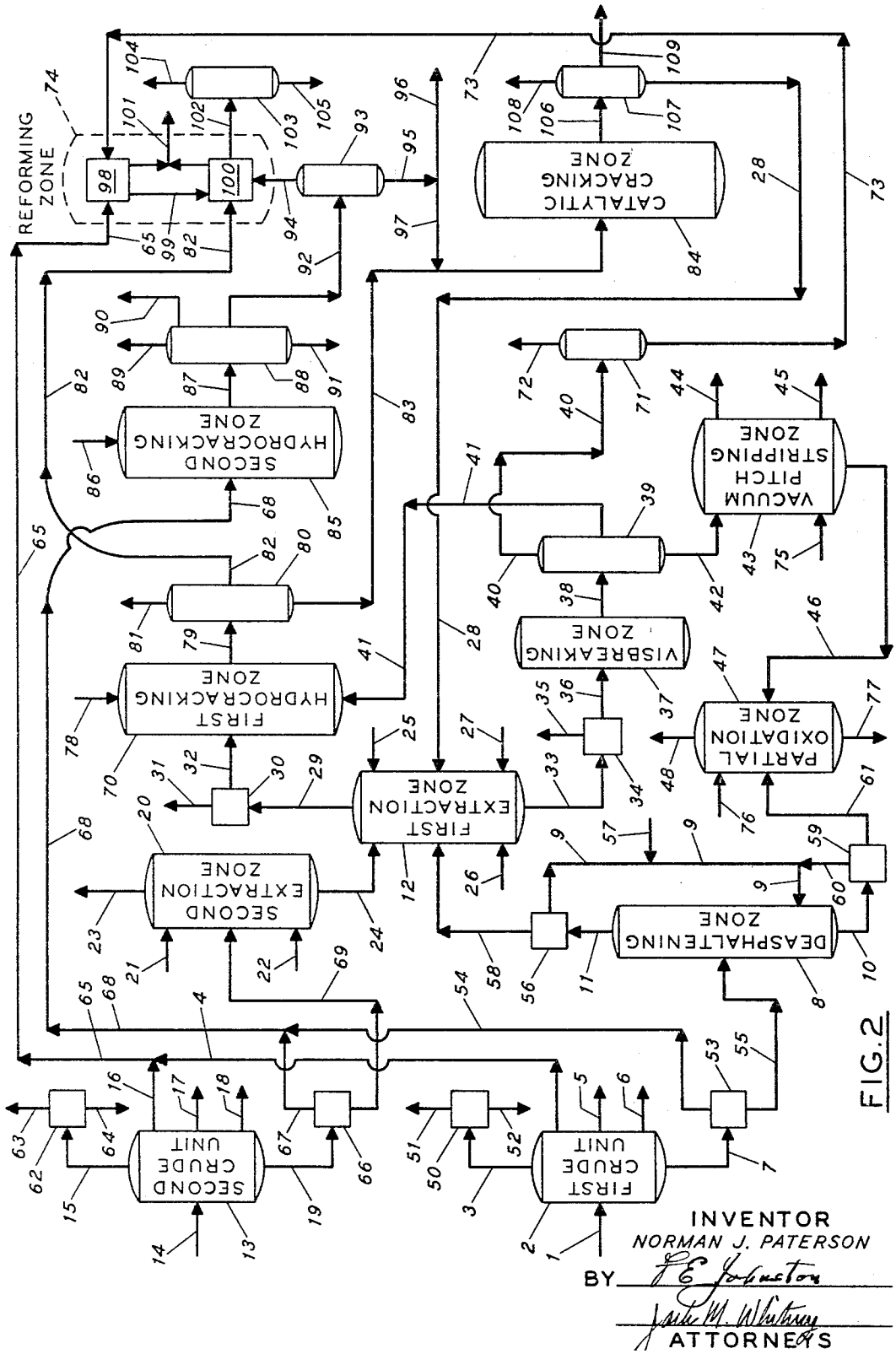

FIG. 2

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COMBINATION EXTRACTION-DEMETALATION PROCESS FOR HEAVY OILS

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ABSTRACT OF THE DISCLOSURE

A process for the production of a low metal content, relatively paraffinic cracking stock and a relatively aromatic stock from which pitch binder oil and carbon black oil may be produced. Asphalt, naphthenic and aromatic oils and solvents from a lubricating oil extraction process are contacted with a deasphaltened metal-containing oil to form a more paraffinic oil and a more aromatic fraction. The latter fraction is visbroken and vacuum pitch stripped. Asphaltenes and pitch stripper bottoms are converted to hydrogen by partial oxidation.

Background of the invention

This invention relates to processes for demetallizing residual oil. More particularly, it relates to processes for producing a low metal content feed of increased paraffinicity suitable for catalytic cracking.

It has heretofore been known that oils having a relatively high content of polynuclear aromatic hydrocarbons are less suitable for cracking than nonaromatic oils since cracking of aromatic-containing oils results in a greater degradation of the oil into undesired products, such as coke and gas, for a given conversion to gasoline than cracking of nonaromatic oils. Thus the ratio of gasoline to coke or gas for a given conversion is higher when cracking nonaromatic oils than when cracking aromatic oils. In view of the foregoing, it has been proposed to remove aromatic constituents from aromatic charge oil before subjecting the same to cracking. Removal of aromatic constituents may be accomplished by treatment of the cracking charge stock with a solvent having a selective solvent power for aromatics as compared with nonaromatics. Such proposed treatment, however, has been relatively expensive due to the necessity for recovering solvent and, accordingly, has not been widely practiced in commercial operation since the improved cracking characteristics of the stock so treated have ordinarily not offset the additional operational costs involved.

In catalytic cracking, it has also been known for some time that certain metals—in particular, iron, nickel and vanadium—are very harmful to cracking catalysts. Deposition on cracking catalysts of concentrations of about 0.1 weight percent or less of such metals causes the production of excessive amounts of coke and gas at the expense of valuable gasoline and heating oil fractions. This leads to an overloading of the regeneration and gas handling equipment and reduces the allowable feed rate to the catalytic cracking units.

There are two principal sources of metallic contamination in catalytic cracking units. The first is erosion of the unit itself. The second source is unfilterable metallic impurities brought in with the feedstock, either in colloidal suspension or particularly as oil-soluble, metallo-organic compounds. It is the removal of this latter type of contaminants with which the present invention is particularly concerned.

It has also been known, prior to the present invention, to improve the qualities of petroleum lubricating oil fractions by extraction with a first solvent having a preferential selectivity for the relatively more aromatic and naphthenic type constituents as compared to the relatively more paraffinic type constituents. In such prior practice, the usual procedure for solvent refining of lubricating oils has been to contact the oil stock undergoing treatment with solvent in an extraction tower. Thus the oil charge is ordinarily introduced into a lower portion of an elongated tower while solvent is introduced into the upper portion thereof. The oil and solvent move countercurrently through the tower, efficient contact between the countercurrently moving phases being generally secured by suitable distributing and contacting means—such as by contact masses, distributing plates, pierced plates, rotating disc contactors, and the like. Temperature and pressure conditions are maintained in the tower to secure the formation of extract and raffinate phases. The phases are separately removed from the tower. Solvents of the class which is suitable for this extractive operation are, for example, furfural, sulfur dioxide, phenol, cresol, aniline, nitrobenzene, beta-beta-dichloroethyl ether (chlorex), and the like. Such solvents may have been further modified with regard to selectivity and solvent power by the addition of, for example, water, alcohols, or glycols. The preferred solvents are phenol and furfural.

In many cases, particularly when a lubricating oil fraction contains very heavy naphthenic or aromatic and asphaltic components, it is desirable to add a second solvent, normally a light paraffin, to aid in separating the two phases. This solvent causes the heavier materials to be rejected into the extract phase, while the solvent is concentrated in the raffinate phase which contains the high-quality lubricating oil.

The products of the treatment of such a lubricating oil fraction with two or more solvents are these: (1) a "lubricating oil extract" which, as the term will hereinafter be used, is defined as the lower viscosity-gravity constant phase of the two phases produced and comprises the major portion of the first (selective) solvent, the minor portion of the second (paraffinic) solvent, and the heavier aromatic and naphthenic components of the lubricating oil fraction; and (2) the raffinate, or higher viscosity-gravity constant phase of the two phases produced, which comprises the more paraffinic components of the lubricating oil feedstock, the minor portion of the first solvent, and the major portion of the second solvent.

It has also been known that the "lubricating oil extract" can be employed directly without removal of either solvent in the extraction of a petroleum oil to be used as a cracking charge stock. The extract and raffinate fractions obtained from this extraction are thereafter separated and the solvents are removed therefrom. The resulting solvent-free raffinate fraction can then be subjected to catalytic cracking, affording a high yield of a product characterized by an improved gasoline/coke ratio.

Summary

It has now been discovered that if the "lubricating oil extract" contains a substantial amount of asphalt as well as the other components described above, this "asphaltic extract" may be used to demetallize a metals-containing petroleum oil while simultaneously separating from the petroleum oil a predominantly more paraffinic catalytic cracking stock.

In broad outline, this invention involves three processing zones and two feedstocks. The first feedstock, which is the metals- and asphaltene-containing petroleum oil boiling substantially entirely above 900° F. which is to be processed, is passed into a deasphaltening zone wherein it is contacted with a C_3–C_8 paraffinic solvent and sep-

arated into two fractions. The heavier or "asphaltene" fraction comprises asphaltenes with a softening point above 300° F. (as measured by the "ball-and-ring" method of ASTM D–36–26) containing a portion of the metalliferous contaminants and a minor portion of the paraffinic solvent. The lighter or "maltene" fraction comprises nonasphaltene materials and the remainder of the metalliferous contaminants. Designation of at least a 300° F. softening point for the heavier phase assures that essentially all the nonasphaltene material will be in the lighter phase. The asphaltene fraction is withdrawn from the deasphaltening zone and may be further processed in a manner to be hereinafter described. The maltene fraction is also withdrawn from the deasphaltening zone and is passed into the central processing zone, which is the first extraction zone, wherein it is contacted with asphalt and other materials also hereinafter described.

The second, or asphaltic, feedstock is a partially naphthenic and aromatic lubricating oil fraction. This feedstock usually differs from the first feedstock in that it is a preferred feedstock for the production of lubricating oils. In addition, it generally contains a higher proportion of components boiling within the range of from about 650°–1,100° F. and has a lower metal content. This feedstock is contacted in a second extraction zone with at least one solvent substantially selective for the extraction of naphthenic and aromatic components from the feedstock and at least one solvent which preferentially concentrates in the lighter phase and rejects asphaltic components into the heavier phase upon phase separation in this zone. The heavier phase is the "asphaltic extract" described hereinbefore. This asphaltic extract is withdrawn from this second extraction zone and passed into the first extraction zone wherein it contacts the maltene fraction from the deasphaltening zone. The asphalt and other components, including the solvents, in the asphaltic extract serve to cause separation of the materials in the first extraction zone into a lower specific gravity, lower metal content, more paraffinic fraction and a higher specific gravity, higher metal content, more aromatic fraction. The lighter fraction contains less than 25 p.p.m. metals (calculated as elemental metal) and may be used as a hydrocracker charge stock. Preferentially it will contain less than 1 p.p.m. metals and may be used as a catalytic cracking charge stock. These fractions are separately removed from the first extraction zone, and the solvents are removed from each.

In a narrower form, the invention comprises the steps recited above followed by thermal visbreaking of the solvent-free, more aromatic fraction at a temperature in the range of from about 650° F. to about 1,000° F. and a pressure in the range of from about 50 to about 1,000 p.s.i.g. This increases the aromaticity of the more aromatic fraction and enhances its ability to produce high-quality carbon black oil and pitch binder base stock in subsequent processing steps.

In a still narrower form, the invention comprises the above steps followed by fractionation of the visbroken material into at least a lighter fraction and a heavier, more aromatic fraction followed by stripping of at least a portion of the latter with steam in a vacuum pitch stripping zone to produce a high-quality carbon black oil and pitch binder base stock.

In a still narrower form, the invention comprises the above steps followed by conversion of at least a portion of the heavier fraction from the vacuum pitch stripping zone and the asphaltene fraction from the deasphaltening zone to hydrogen by reacting in the presence of oxygen in a partial oxidation zone comprising at least a gas generator, a shift converter and carbon dioxide removal means. The hydrogen so produced can be used in the hydrogen-consuming units in the refining system, thereby making the system for processing the various oil fractions here produced at least partially self-sufficient.

Brief description of the drawings

FIGURE 1 illustrates the process of this invention in its both broadest form and successively narrower embodiments; and

FIGURE 2 illustrates the embodiment of the example which will be presented hereinafter and shows how the process of this invention may be incorporated into an overall refining scheme.

Description of the preferred embodiments

FIGURE 1 illustrates the process of this invention in its broadest form. A petroleum feedstock, which may be a crude oil, shale oil, topped crude or similar material, enters through line **1** to first crude unit **2** wherein it is fractionated into a plurality of materials of increasing boiling point. The lightest of these materials is removed through line **3**, and successively higher boiling and heavier materials are removed through lines **4**, **5** and **6**. The remaining materials which boil above 900° F. are withdrawn from the bottom of first crude unit **2** through line **7** and are passed into deasphaltening zone **8** wherein they are contacted with a C_3–C_8 paraffinic solvent which enters deasphaltening zone **8** through line **9**. A detailed description of deasphaltening zone **8**, as well as a detailed description of the other processing zones, will be presented hereinafter.

In deasphaltening zone **8**, the 900° F.+ bottoms material is separated into two fractions on contact with the paraffinic solvent. The asphaltene fraction is withdrawn through line **10** for further processing hereinafter described. The maltene fraction, which may include the major portion of the paraffinic solvent, is withdrawn through line **11** and passed to first extraction zone **12**.

A second feedstock, which must contain asphalt and other naphthenic components, enters second crude unit **13** through line **14**. This feedstock is fractionated to remove the light components in a manner similar to that described for first crude unit **2**. The lightest material is taken off overhead through line **15**, and successively higher and heavier boiling materials are removed through lines **16**, **17** and **18**. The heaviest material which contains all the asphalt and lubricating oil components is withdrawn from second crude unit **13** through line **19** and passed to second extraction zone **20** wherein it is contacted with a first solvent selective for the extraction of the more aromatic and naphthenic components and a second solvent which causes rejection of the asphalt into the extract or heavier phase. The first solvent, which enters through line **21**, may be furfural, phenol, or other commonly known similar materials. The second solvent, which enters through line **22**, may be propane, butane, or other light paraffin. The major portion of the lubricating oil components, along with the major portion of the second solvent, is removed overhead through line **23** and passed to further processing, not herein shown.

The extracted materials, along with the solvents and asphalt, which altogether comprise the "alsphaltic extract," are removed from second extraction zone **20** through line **24** and are passed into first extraction zone **12** wherein they contact the maltene fraction. For final control purposes, it may be desirable to add fresh selective solvent to zone **12** through line **25** to aid in removing substantially the last traces of the aromatic and naphthenic materials. Similarly, it may be desirable to add fresh paraffinic solvent through line **26** to promote complete separation of the paraffinic materials which may have been carried over from second extraction zone **20**. Water may be added to zone **12** through line **27** to raise the miscibility temperature of the solvent system and to assist in the separation of additional paraffinic type oil. Optionally, a small amount of cycle oil from a downstream catalytic cracker may also be added to zone **12** through line **28** in a manner which will be more fully described in the discussion of FIGURE 2.

In first extraction zone **12**, the combined materials

separate into two fractions: a more paraffinic fraction suitable for use as a catalytic cracking stock and a more aromatic fraction suitable for processing as hereinafter described. The presence of the asphaltic extract from the second extraction zone promotes simultaneous demetallizing by extraction of the organo-metallic compounds so that the predominantly paraffinic fraction is improved in its characteristics as a catalytic cracking stock in that it contains less than 25 p.p.m. of metals. This low metal content, more paraffinic material is removed along with a portion of the combined solvents through line 29. The solvents are separated in zone 30, removed through line 31 and may be recycled by means not shown for reuse in the various processing zones of this invention. The solvent-free, more paraffinic material is passed on through line 32 for further processing, preferably of the type described hereinafter in the discussion of FIGURE 2.

The predominantly aromatic fraction, which contains the remaining metals, is withdrawn from zone 12 through line 33 along with the remaining solvents. The solvents are separated in zone 34, removed through line 35 and may be recycled through means not shown for reuse in the various processing zones of the invention. The solvent-free, metals-containing, more aromatic fraction is passed on through line 36 for further processing in the manner described hereinafter.

The process of this invention is characterized in narrower form by the successive steps also shown in FIGURE 1. After the processing described above, the solvent-free, metals-containing, predominantly aromatic fraction recovered from first extraction zone 12 is passed through line 36 to visbreaking zone 37 wherein mild thermal cracking of the heavy materials occurs. The partially thermally cracked effluent of visbreaking zone 37 is passed through line 38 to fractionation zone 39 wherein the lighter materials are separated into at least two fractions and are removed into a plurality of lines, such as lines 40 and 41. The preferred further processing of these fractions is described hereinafter in the discussion of FIGURE 2. The remaining heavy, visbroken, more aromatic material is withdrawn from the bottom of fractionation zone 39 through line 42 and passed into vacuum pitch stripping zone 43 wherein additional materials are separated. These materials, such as a particularly high-quality carbon black oil and pitch binder base stock, are removed through a plurality of lines, such as 44 and 45.

The remaining heavy material, which now comprises predominantly undesirable asphalts and metals, is withdrawn from zone 43 through line 46. If necessary, the pitch binder base stock may be oxidized and/or heat treated to meet designated specifications. In addition, colloidal carbon in an amount not exceeding 15 weight percent of the pitch binder base stock may be added to line 45 by conventional means not shown. Preferably, however, the heavy material is passed into partial oxidation zone 47. The asphaltene fraction from deasphaltening zone 8, which has been withdrawn from that zone through line 10, is also passed into partial oxidation zone 47. The combined materials are then reacted in the presence of oxygen to produce hydrogen which is withdrawn through line 48. If desired, all or a portion of the heavy bottoms from vacuum pitch stripping zone 43 may be withdrawn from line 46 through line 49 and passed to further processing, such as fluid or delayed coking. The metals may be recovered from the fly ash resulting from combustion of the coke; for instance, as a power plant fuel.

The deasphaltening zone may be a batch operation, a multiple vessel operation or preferably a substantially continuous liquid-liquid countercurrent treating operation. The residuum to be deasphaltened is generally introduced near the bottom of the deasphaltening tower and flowed therein in countercurrent liquid-liquid contact with a suitable deasphaltening solvent. The solvent used in this process may be any one or more of the C_3–C_8 paraffins, such as propane, isobutane, n-pentane, isooctane, cyclohexane or methylcyclopentane. The heavier paraffins are preferred for they produce higher yields of the deasphalted maltenes. In a multiple vessel operation, different solvents may be used in different vessels.

The deasphaltening operation is carried out at any suitable deasphaltening temperature and pressure. The temperature and pressure are adjusted so as to maintain the deasphaltening solvent in the liquid phase during the deasphaltening operation. A deasphaltening temperature in the range of 125°–600° F., usually not more than 75° F. lower than the critical temperature of the deasphaltening solvent, and a pressure in the range of 200–1,000 p.s.i.g. are employed depending on the composition of the deasphaltening solvent and the composition of the residuum undergoing deasphaltening. The solvent-to-residuum volume ratio is in the range of 2:1 to 10:1. The deasphaltening tower may be operated isothermally or under a temperature gradient with the top tower temperature lower than the bottom tower temperature but not more than about 75° F. If the residuum is deasphaltened in a series of towers, the above considerations apply to each tower in the series with, of course, appropriate adjustments in operating conditions for the changing composition of the material being treated and the solvent being used in each tower.

All or part of the solvents used in the deasphaltening zone may be removed from either or both the maltene and asphaltene fractions by conventional solvent removal means before further processing of the fractions, but this solvent removal is not required. Any solvent remaining in the maltene fraction will aid in the paraffinic-aromatic separation in the first extraction zone and will be removed from the products of that zone by the solvent removal operations heretofore described.

The first extraction zone is a vessel suitable for liquid-liquid contacting between the maltene fraction from the deasphalting zone and the asphaltic extract from the second extraction zone. Preferably, it is a vessel suitable for effecting continuous countercurrent liquid-liquid contacting. The zone is operated at a temperature in the range of 100°–350° F. and a pressure in the range of 100–800 p.s.i.g. The temperature and pressure are adjusted to maintain all the materials in the liquid phase during contacting. Operation may be isothermal; but, preferably, there will be a temperature gradient with the region at the top of the vessel no more than 100° F. hotter than that at the bottom. Preferably the extract from the second extraction zone enters the first extraction zone near the top of the latter and descends while contacting the maltene fraction from the deasphaltening zone which entered nearer the bottom of the first extraction zone. Any additional streams, such as those supplying additional selective solvent or paraffinic solvent or similar substitutes for either or both of these, or water, may be added to the zone by conventional means and at easily determined appropriate points in the vessel. It may also be desirable to add some heavy gas oil or other nonasphaltic heavy oil, such as FCC cycle oil, in order to increase overall product yields when the process of this invention is integrated into an overall refining processing scheme.

The second extraction zone may be any conventional type of lubricating oil extract apparatus, such as a single vessel, for extracting a long residuum, or a plurality of vessels, each extracting a narrow cut from distillation of crude oil, followed by blending of the extracts from each narrow cut. The principal requirement as far as the process of this invention is concerned is that the asphaltic extract from the second extraction zone contain at least the asphaltic materials and a portion of the selective solvent from the extract. This means that when multiple vessel extraction is used, the extract and at least a portion of the solvent from the extraction of the heaviest narrow cut will comprise the materials termed "asphaltic extract" passed to the first extraction zone. Extracts and solvents

from the extraction of one or more of the lighter, narrow cuts may also be included among the materials passed to the first extraction zone.

FIGURE 2 illustrates an example of the process of this invention integrated into an overall refinery processing scheme. The crude to be treated, which comprises 164,000 b.p.d. of a 21.5° API Los Angeles Basin California crude, enters first crude unit **2** through line **1** and is separated into five fractions. The lightest fraction is removed through line **3** and passed to separation zone **50** wherein it is separated into 935 b.p.d. of C_3— EFO (equivalent fuel oil), which is removed through line **51**, and 3,850 b.p.d. of C_4 to 200° F. light, straight-run gasoline, which is removed through line **52**. From the upper portion of the crude distillation column, 15,400 b.p.d. of 200°–350° F. heavy, straight-run gasoline is withdrawn through line **4**. This material is joined with similar material from second crude distillation unit **13** and is passed to catalytic reforming as hereinafter described. At an intermediate point in the distillation column, 8,950 b.p.d. of 350°–525° F. jet fuel is withdrawn through line **5**. From the lower portion of the column, 7,000 b.p.d. of 525°–600° F. diesel fuel is withdrawn through line **6**. The remaining heavy material is withdrawn from the bottom of the crude unit and is passed through line **7** to separation zone **53** wherein there are separated under vacuum 77,765 b.p.d. of 600°–1,025° F. gas oil which are removed through line **54** and passed, after being joined with similar material from second crude distillation zone **13**, to subsequent hydrocracking, hereinafter described. The remaining material amounting to 50,000 b.p.d. of 5.2° API, 1,025° F.+ residuum containing 180 p.p.m. of nickel, 175 p.p.m. of vanadium and 100 p.p.m. of iron is withdrawn from separation zone **53** and passed to deasphaltening zone **8** through line **55**.

Separation zone **53** comprises conventional apparatus suitable for separation of the heavy bottoms material from the first crude unit into the gas oil fraction and the heavier residual fraction. It is preferred that the apparatus be operated under a vacuum.

Deasphaltening zone **8** is operated with a temperature gradient of 50° F. The solvent, 2,757,500 lb./hr. of n-pentane, is introduced through line **9** near the bottom of the deasphaltening column where the column temperature is 300° F. and contacts the residuum countercurrently. The maltene fraction is removed overhead from the column through line **11** along with the major portion of the n-pentane solvent. The asphaltene fraction is withdrawn from the bottom of the column along with a minor portion of the n-pentane solvent through line **10**. The solvent and maltene fraction are separated in zone **56**, and the separated solvent is recycled through line **9** to the deasphaltening zone. Additional make-up solvent may be added to line **9** through line **57** if necessary. After solvent removal, 37,500 b.p.d. of the solvent-free maltene fraction with a gravity of 8.7° API and containing 100 p.p.m. of nickel, 58 p.p.m. of vanadium and 30 p.p.m. of iron are passed through line **58** to first extraction zone **12**. The asphaltene fraction and solvent may be separated in zone **59**. The asphaltene fraction and solvent may be separated in zone **59**, and the separated solvent is recycled through line **60** to line **9** and deasphaltening zone **8**. Twelve thousand five hundred b.p.d. of the solvent-free asphaltene fraction with a gravity of —4.2° API a softening point of 380° F. (as measured by the ball-and-ring method of ASTM D–36–26) and containing 68.8 weight percent asphaltenes are withdrawn through line **61** and passed to partial oxidation zone **47**.

The asphaltic extract to be used as the demetallizing agent comes from a second crude oil. Fifty thousand b.p.d. of asphalt-containing crude oil, segregated for recovery of its superior lube oil base stock components, a 33.0° API mixture of San Joaquin Valley California crude and Four Corners Utah crude, are passed into second crude unit **13** through line **14**. In crude unit **13**, the crude is separated into a plurality of fractions. The lightest fraction is withdrawn overhead through line **15** and is passed to stabilizer **62** wherein it is separated into 700 b.p.d. of C_3–EFO, which are withdrawn through line **63**, and 3,700 b.p.d. of C_4 to 200° F. light straight-run gasoline, which are withdrawn through line **64**. Near the top of crude unit **13**, 6,600 b.p.d. of 200°–350° F. heavy straight-run gasoline are withdrawn through line **16**. The material is joined with similar material withdrawn from first crude unit **2** through line **4** and is passed to catalytic reforming through line **65** as hereinafter described. At an intermediate point in the crude unit **13**, 12,050 b.p.d. of 350°–525° F. jet fuel are withdrawn through line **17**. Near the bottom of crude unit **13**, 3,260 b.p.d. of 525°–600° F. diesel fuel are withdrawn through line **18**. The asphalt-containing heavy bottoms is withdrawn from the bottom of crude unit **13** through line **19** and is passed to separation zone **66**, which comprises a vacuum distillation column, wherein 8,890 b.p.d. of 600°–725° F. as oil are separated. This gas oil is withdrawn through line **67** and is blended with the gas oil from separation zone **53**. The combined gas oil streams are then passed to hydrocracking, hereinafter described, through line **68**.

Through line **69**, 14,800 b.p.d. of asphalt-containing 725° F.+ residuum with a gravity of 16.5° API are withdrawn from zone **66** and passed to second extraction zone **20** wherein they are contacted with 541,160 pounds per hour of phenol, which enters through line **21**, and 344,000 pounds per hour of propane which enters through line **22**. A high-quality lubricating oil is withdrawn through line **23**. The stream being withdrawn through line **23** contains 7,030 b.p.d. of the lubricating oil with a gravity of 29.9° API and a metals content of 0.09 p.p.m. nickel, 0.04 p.p.m. vanadium, 0.46 p.p.m. sodium and 0.16 p.p.m. iron, along with 193,400 pounds per hour of propane and 64,000 pounds per hour of phenol. The phenol and propane are separated from the lubricating oil by conventional solvent removal means not shown.

The remaining material in zone **20** is termed the "asphaltic extract" and comprises 7,770 b.p.d. of an extract oil with a gravity of 6.1° API and containing asphalt, 30 p.p.m. nickel, 14 p.p.m. vanadium, 25 p.p.m. of sodium and 12 p.p.m. of iron, along with 477,160 pounds per hour of phenol and 150,600 pounds per hour of propane. This extract is withdrawn through line **24** and passed to first extraction zone **12**.

The asphaltic extract enters zone **12** near the top and passes downward, contacting the maltenes which have entered nearer the bottom and are flowing upward. The top column temperature is maintained at 160° F. and the bottom column temperature at 130° F. The pressure is 300 p.s.i.g. Fifty thousand pounds per hour of anhydrous phenol are added through line **25**, 100,000 pounds per hour of propane are added through line **26**, and 25,000 pounds per hour of water are added through line **27**. Ten thousand b.p.d. of 750°–950° F. FCC cycle oil, which may include small amounts of catalyst fines and other foreign material, are withdrawn from the bottom of an FCC unit, hereinafter described, and passed into zone **12** through line **28**. The products of zone **12** are an overhead fraction which comprises 43,050 b.p.d. of a more paraffinic raffinate oil (which contains 7 p.p.m. nickel, 3 p.p.m. vanadium, 1 p.p.m. sodium and 2 p.p.m. iron), 5,000 pounds per hour of water, 62,000 pounds per hour of phenol and 141,000 pounds per hour of propane; and a bottoms fraction which comprises 12,220 b.p.d. of a predominantly aromatic extract oil, 445,160 pounds per hour of phenol, 109,600 pounds per hour of propane and 20,000 pounds per hour of water. The paraffinic fraction is withdrawn overhead through line **29** and passed to solvent separation zone **30** wherein the water, propane and phenol are separated by conventional means and withdrawn through line **31**. If desired, the materials withdrawn through line **31** may be separated and recycled by means not shown for use in second extraction zone

20 or first extraction zone 12. The solvent-free, predominantly paraffinic oil, which has a gravity of 12.9° API, is passed through line 32 into first hydrocracking zone 70. The aromatic bottoms fraction is withdrawn from zone 12 through line 33 and is passed to solvent separation zone 34 wherein the phenol, water and propane are separated by conventional means and withdrawn through line 35. These materials may be separated and recycled in the same manner as described for the materials withdrawn from zone 39 through line 31.

The solvent-free aromatic oil, which has a gravity of −4.7° API, is withdrawn from zone 34 through line 36 and passed to visbreaking zone 37. Zone 37 is a conventional once-through, thermal visbreaking zone comprising a tubular reaction zone which is operated at a temperature in the range of 890°–910° F. and a pressure of 200 p.s.i.g. to produce mild cracking of the heavy aromatic oil, thus concentrating the aromatic content still further by cracking out the nonaromatic material, and a quenching zone wherein the visbroken material is quenched to a temperature of 775° F. and the pressure is reduced to 100 p.s.i.g. This material is then passed through line 38 into separator 39 wherein it is separated into three fractions. The lightest fraction, which comprises 3,220 b.p.d. of 400° F.— materials, is withdrawn overhead through line 40 and passed to separator 71 wherein it is separated into 1,220 b.p.d. of C_4— materials and 2,000 b.p.d. of C_5 to 400° F. catalytic reformer feed. The C_4— material is withdrawn through line 72 and is recovered or passed for further processing by means not shown. The catalytic reformer feed is withdrawn through line 73 and passed to the first stage of catalytic reformer zone 74, hereinafter described. At an intermediate point in separation zone 39, 2,000 b.p.d. of 400°–650° F. hydrocracker feed are withdrawn through line 41 and passed to first hydrocracking zone 70. The remaining material, which comprises 7,470 b.p.d. of 650° F.+ highly aromatic materials, is withdrawn through line 42 and passed to vacuum pitch stripping zone 43 wherein it is separated by contact with steam which enters zone 43 through line 75 into 2,500 b.p.d. of 650°–850° F. carbon black oil, 2,480 b.p.d. of 850°–1,050° F. pitch binder base stock and 2,490 b.p.d. of 1,050° F.+ heavy bottoms material. The carbon black oil is withdrawn through line 44 and recovered by conventional means not shown. The pitch binder base stock is withdrawn through line 45 and similarly recovered, and the heavy bottoms material is withdrawn through line 46 and passed to partial oxidation zone 47.

Partial oxidation zone 47 is a conventional unit comprising at least a gas generator, a shift converter and CO_2 removal facilities. The heavy materials, which enter through lines 46 and 61, are heated and reacted with a stoichiometric deficiency of oxygen, which enters through line 76, forming a $C\text{-}H_2$ rich gas which is shift converted to produce 230 $\overline{M}$ SCFD of high-purity hydrogen. This hydrogen is withdrawn through line 48 and is passed through means not shown to various hydrogen-consuming units in the system. Metallic contaminants and other ash, which are not converted to hydrogen, carbon monoxide or carbon dioxide, are removed from partial oxidation zone 47 through line 77. Where the initial crude being treated contains a large amount of metals, it may be economically desirable to recover the metals from the ash by conventional means not shown.

The solvent-free paraffinic material in line 32 and the 400°–650° F. visbroken material in line 41 are passed into first hydrocracking zone 70 wherein they are contacted with hydrogen and a sulfactive hydrogenation catalyst at elevated temperature of 700–900° F. and pressure of 1,500–4,000 p.s.i.g. The hydrocracking zone serves to remove substantially all the remaining metal contaminants and to convert at least 30 percent of the 900° F.+ oil to material boiling below 900° F. Suitable catalysts for use in zone 70 include the sulfactive hydrogenation catalysts of no more than moderate acidity, comprising combinations of Group VI and Group VIII metals, their oxides and their sulfides, especially nickel sulfide together with molybdenum sulfide or tungsten sulfide, associated with an inorganic refractory oxide carrier, such as alumina, silica-alumina, silica-magnesia, and the like. Strongly acidic hydrocracking catalysts, such as those comprising Group VIII metals, their oxides and sulfides, associated with an active silica-alumina cracking catalyst carrier wherein silica is a major component, are not suitable because they rapidly lose their activity and do not exhibit sufficient hydrogenation activity at the conditions employed. Hydrogen in an amount of 64 $\overline{M}$ SCFD is added to zone 70 through line 78. This hydrogen may be supplied from partial oxidation zone 47, catalytic reformer zone 74, or any other hydrogen source. The hydrocracked oil is passed through line 79 to separation zone 80 wherein it is separated into three principal fractions. The lightest fraction, which comprises 430 b.p.d. of mixed butanes is withdrawn overhead through line 81. At an intermediate point in separator 80, 2,115 b.p.d. of C_5 to 370° F. reformer feed is withdrawn through line 82 and passed to the second stage of reforming zone 74. The remaining heavy hydrocracked material, which comprises 45,070 b.p.d. of 370°–850° F. material, is withdrawn from the bottom of separator 80 and passed through line 83 to catalytic cracking zone 84.

The 86,555 b.p.d. straight-run gas oil separated in zones 53 and 66 is passed into second hydrocracking zone 85 through line 68. Second hydrocracker zone 85 comprises a denitrification stage and a hydrocracking stage. In the denitrification stage, the feed to the hydrocracking process is contacted with hydrogen in the presence of a suitable hydrogenation catalyst at elevated temperatures and pressures to remove nitrogen compounds therefrom. A particularly effective catalyst for removing nitrogen by hydrogenation is one wherein a coprecipitated molybdena-alumina material (e.g., one prepared in accordance with the disclosure of U.S. Patent No. 2,432,286 to Claussen et al. or U.S. Patent No. 2,697,066 to Sieg) is combined with cobalt oxide, the final catalyst having a metals content equivalent to about 2 percent cobalt and 7 percent molybdenum. Other suitable catalysts include those mentioned in the previous paragraph. Representative processing conditions for removing nitrogen with this catalyst are an LHSV of 1–3, temperature of about 700°–850° F., pressure of about 200–3,000 p.s.i.g. and 1,000–15,000 s.c.f. of hydrogen per barrel of feedstock.

The resulting effluent is treated in accordance with methods presently known in the art so as to remove ammonia and some hydrogen sulfide which may be present. A preferred removal method involves injecting water into the total effluent from the hydrofining unit and then passing the resulting mixture into a high-pressure separator operating under such conditions of temperature and pressure (for example, 100° F. and 950 p.s.i.g.) that a gaseous overhead is removed that is predominantly hydrogen, but which normally contains some hydrogen sulfide and light hydrocarbons. This overhead (following a clean-up treatment to remove any nitrogen and sulfur-containing compounds, if desired) can be recycled to the denitrification unit along with make-up hydrogen. Two liquid phases are formed in the separator, an upper hydrocarbon phase and a lower aqueous phase which contains essentially all of the ammonia present and some hydrogen sulfide in the form of ammonium sulfide. The aqueous phase is removed from the system and discarded.

The hydrocarbon layer is then preferably passed into a stripper or distillation column from which any remaining hydrogen sulfide, ammonia and water are removed overhead. The stream may also be freed of any light hydrocarbon fractions (boiling in the gasoline range or below) formed as a result of hydrocracking reactions taking place over the hydrofining catalyst.

The portion of the denitrified feed to be hydrocracked, along with from about 1,500–30,000, and preferably from

about 3,000–15,000, standard cubic feet (s.c.f.) of hydrogen per barrel of total reaction feed, is passed into the hydrocracking zone at a liquid hourly space velocity (LHSV) of from about 0.2 to 15, and preferably from about 0.4 to 3.0, and intimately contacted with the catalyst.

The catalyst employed in the hydrocracking zone is one wherein a material having hydrogenating-dehydrogenating activity is deposited or otherwise disposed on an active cracking catalyst support. The cracking component may comprise any one or more of such acidic materials as silica-alumina, silica-magnesia, silica-alumina-zirconia composites, alumina-boria, fluorided composites, and the like, as well as various acid-treated clays, zeolites, and similar materials. The hydrogenating-dehydrogenating components of the catalyst can be selected from any one or more of the various groups VI, VII and VIII metals, as well as the oxides and sulfides thereof, alone or together with promoters and stabilizers that may have by themselves small catalytic effect, representative materials being the oxides and sulfides of molybdenum, tungsten, vanadium, chromium, and the like, as well as of metals, such as iron, nickel, cobalt and platinum. If desired, more than one hydrogenating-dehydrogenating component can be present; and good results may be obtained with catalysts containing composites of two or more of the oxides of molybdenum, cobalt, chromium, tin and zinc, and with mixtures of said oxides with fluorine. The amount of the hydrogenating-dehydrogenating component present can be varied within relatively wide limits of from about 0.5–30 percent based on the weight of the entire catalyst.

The contacting step is conducted under a pressure of at least 500 p.s.i.g., and preferably from about 800–3,000 p.s.i.g. The temperature is preferably maintained in the range of from about 400°–750° F.; because, at temperatures above about 750°–800° F., the amount of gasoline product lost to the less desirable C_3 and lighter materials rapidly increases, thus lowering the motor fuel yield. For example, it has been found that the amount of methane produced at 800° F. per unit of converted product is approximately sixteen times as great as that formed at 700° F. and four times as great as that produced at 750° F. At higher temperatures, the situation becomes much worse. With operation at 800° F. and higher with the same and similar feeds, but with nickel sulfide on silica-alumina, regeneration is required after on-stream periods of a few hundred hours or less, compared with operation below 700° F., with which can be obtained on-stream periods of several thousand hours without regeneration. In the present process, it is recommended that the reaction be conducted at an initial on-stream temperature from about 500–650° F., with a progressive increase to about 750° F. so as to maintain catalyst activity at a controlled level. The initial and terminal temperatures will vary, with character of feed and catalyst, within the overall range specified above.

Total hydrogen required to process the gas oil is 200 $\overline{M}$ SCFD, which may be supplied through line **86** from partial oxidation zone **47**, catalytic reformer **74**, or any other hydrogen source. The hydrocracked material from second hydrocracking zone **85** is withdrawn through line **87** and passed to separation zone **88** wherein it is separated into four fractions. The lightest fraction, which comprises 16,800 b.p.d. of C_4— material is withdrawn overhead through line **89**. A second fraction comprising 25,000 b.p.d. of C_5 to 180° F. gasoline is withdrawn through line **90**. The heaviest fraction comprising 10,000 b.p.d. of 390°–525° F. material is withdrawn from the bottom of zone **88** through line **91**. A fourth fraction, comprising 50,500 b.p.d. of 180°–390° F. material, is withdrawn from the lower portion of zone **88** through line **92** and is passed into splitter **93** wherein it is separated into two fractions. The lighter fraction, comprising 37,500 b.p.d. of 180°–320° F. material, is withdrawn overhead through line **94** and passed to reforming zone **74**. The heavier fraction, comprising 13,000 b.p.d. of 320°–390° F. material comprising 10 percent paraffins, 65 percent naphthenes and 25 percent aromatics and with a leaded F–1 octane number of 70, is withdrawn from the bottom of splitter **93** through line **95** and may be withdrawn entirely or in part from the system through line **96** and recovered by conventional means not shown. However, in this example, this 320°–390° F. material is passed through line **97** to line **83** and then to catalytic cracking zone **84**.

Catalytic reforming zone **74** is a conventional two-stage reformer in which the first stage is utilized primarily as an olefin saturation, nitrogen- and sulfur-removal unit and the second stage serves as the actual reforming unit. For this reason, the straight-run naphthas from crude units **2** and **13**, which contain some nitrogen and sulfur, are passed through line **65** to first stage **98** of reforming zone **74**. Similarly, the nitrogen-, olefin- and sulfur-containing visbroken material from separation zone **71** is passed through line **73** to first stage **98**. After removal of the sulfur and nitrogen and saturation of the olefins, the combined materials are passed through line **99** to second stage **100** of reforming zone **74**, wherein they are combined with the nitrogen- and sulfur-free hydrocracked materials in lines **82** and **94**.

The reforming zone is operated at conventional reforming conditions including temperatures of about 700° to about 1,050° F., preferably between about 725° and about 1,000° F. The LHSV will vary between about 0.1 and about 10, preferably between about 0.5 and 4. The hydrogen pressure will vary between about 100 p.s.i.g. and about 1,000 p.s.i.g., preferably between about 250 and 750 p.s.i.g. The molar ratio of hydrogen to hydrocarbon charge will vary between about 1 and 20, preferably between about 4 and 12.

The reforming operation is carried out in the presence of hydrogen and a suitable reforming catalyst. Such catalysts include the metals and compounds, such as the oxides and/or sulfides of the metals of the left-hand column of Groups VI and VIII of the Periodic Table of the Elements. The catalyst compounds can be used alone or on a suitable support. Catalysts that comprise platinum or palladium metal deposited on supports, such as alumina, halogen-activated alumina, and the like, are particularly suitable. Silica-alumina, silica-zirconia, and alumina boria are also suitable.

In the reforming process, there is net production of 58.4 $\overline{M}$ SCFD of hydrogen. This net production of hydrogen may be removed through line **101** and used all or in part to supply the hydrogen requirements for the hydrocracking zone.

The reformed, combined materials are withdrawn from second stage **100** of reforming zone **74** through line **102** and are passed into separator **103**, wherein they are separated into a plurality of fractions including 2,460 b.p.d. of butane and lighter hydrocarbons and 55,200 b.p.d. of C_5+ reformate which has a leaded F–1 octane number of 102.55. The butane and lighter hydrocarbon stream are withdrawn through line **104** and are recovered by conventional means not shown. The C_5+ reformate is withdrawn through line **105** and is similarly recovered.

Catalytic cracking zone **84** is a conventional catalytic cracking unit. Preferably it is of the well-known fluid bed type or the gas lift or bucket elevator type wherein a cracking catalyst, such as zeolites or silica-alumina powder or pellets, is continuously circulated between a reaction zone and a regeneration zone, using conversion conditions of 850–1,100° F. and regeneration conditions of 900–1,150° F. at near atmospheric pressure. The manner of controlling the catalytic cracking process, primarily by means of the catalyst circulation rate and feed preheat temperature, to maintain a balance between the heat released by burning coke from the catalyst in regeneration and the heat absorbed by the cracking reactions is well known.

The materials which enter zone 84 through lines 83 and 97 are converted into cracked materials which are withdrawn through line 105 and passed into separator 107, wherein they are separated into three fractions. The lightest, which comprises 11,070 b.p.d. of C_4- materials, is withdrawn overhead through line 108 and recovered by conventional means not shown. The bulk of the cracked materials, which comprises 39,000 b.p.d. C_5 to 430° F. substantially olefin-free materials comprising 60 percent aromatics, 10 percent paraffins and 30 percent naphthenes and having an F–1 leaded octane number of 99.5, is withdrawn through line 109 and similarly recovered. The remaining material, which comprises 10,000 b.p.d. of FCC cycle oil with a gravity of 10.3° API, is withdrawn from the bottom of zone 107 and recycled through line 28 to first extraction zone 12.

From the initial 214,000 b.p.d. of crude oil processed, the following products are obtained:

TABLE I

Product:	Yield (b.p.d., except where noted)
C_3— EFO	1,635
Butanes and lighter hydrocarbons	2,890
Gasoline	126,750
Jet fuel	21,000
Diesel oil	10,260
Lubricating oil	7,030
Pitch binder base stock	2,480
Carbon black oil	2,500
Hydrogen (24 $\overline{M}$ s.c.f.d. net).	

It can be seen that this process thus produces a high yield of very desirable hydrocarbon products with only a small loss to light gases.

The above-described flow system and operating conditions are given for illustrative purposes only. It is apparent that many widely different embodiments of this invention may be made without departing from the scope and spirit thereof and, therefore, it is not intended to be limited except as indicated in the appended claims.

What is claimed is:

1. A process for the demetalization of a petroleum oil boiling above 900° F. and containing asphaltenes and metalliferous contaminants, which comprises:

(a) contacting said oil with a C_3–C_8 paraffinic solvent in a deasphaltening zone under conditions such that said oil is separated in said deasphaltening zone into an asphaltene fraction comprising asphaltenes with a ring-and-ball softening point above 300° F. containing a major portion of the metalliferous contaminants and a minor portion of said paraffinic solvent, and a maltene fraction comprising nonasphaltene materials and the remainder of said metalliferous contaminants, withdrawing from said deasphaltening zone said asphaltene fraction, and withdrawing from said deasphaltening zone said maltene fraction and passing said maltene fraction to a first extraction zone;

(b) contacting in a second extraction zone a partially asphaltenic lubricating oil stock with at least one solvent substantially selective for the extraction of aromatic and naphthenic components from said stock and at least one solvent substantially selective for the separation of asphaltic components from said stock;

(c) withdrawing from said second extraction zone an asphaltic extract comprising the major portion of said selective solvents, asphaltenic components, and a portion of the aromatic and naphthenic oil present in said stock, passing said asphaltic extract into said first extraction zone, and contacting in said first extraction zone said asphaltic extract and said maltene fraction; and

(d) separating said contacted materials in said first extraction zone into a predominantly paraffinic fraction containing less than 25 p.p.m. metalliferous contaminants and a predominantly aromatic fraction containing the remainder of said metalliferous contaminants and withdrawing said paraffinic fraction and said aromatic fraction separately from said first extraction zone, removing said selective solvent from each of said fractions, and recovering separately said solvent-free paraffinic fraction and said solvent-free aromatic fraction.

2. The process of claim 1 wherein said solvent-free aromatic fraction withdrawn from said first extraction zone is thermally cracked in a thermal visbreaking zone at a temperature in the range of from about 650° F. to about 950° F. and a pressure in the range of from about 50 to about 1,000 p.s.i.g.

3. The process of claim 2 wherein the product of said visbreaking zone is fractionated into a plurality of fractions including a more aromatic fraction, and at least a portion of said more aromatic fraction is contacted with steam in a pitch stripping zone at less than atmospheric pressure to produce a pitch binder base stock.

4. The process of claim 3 wherein at least a portion of said more aromatic fraction from said visbreaking zone and said asphaltene fraction from said deasphaltening zone are converted to hydrogen by reacting in the presence of oxygen in a partial oxidation zone comprising at least a gas generator, a shift converter, and carbon dioxide removal means.

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