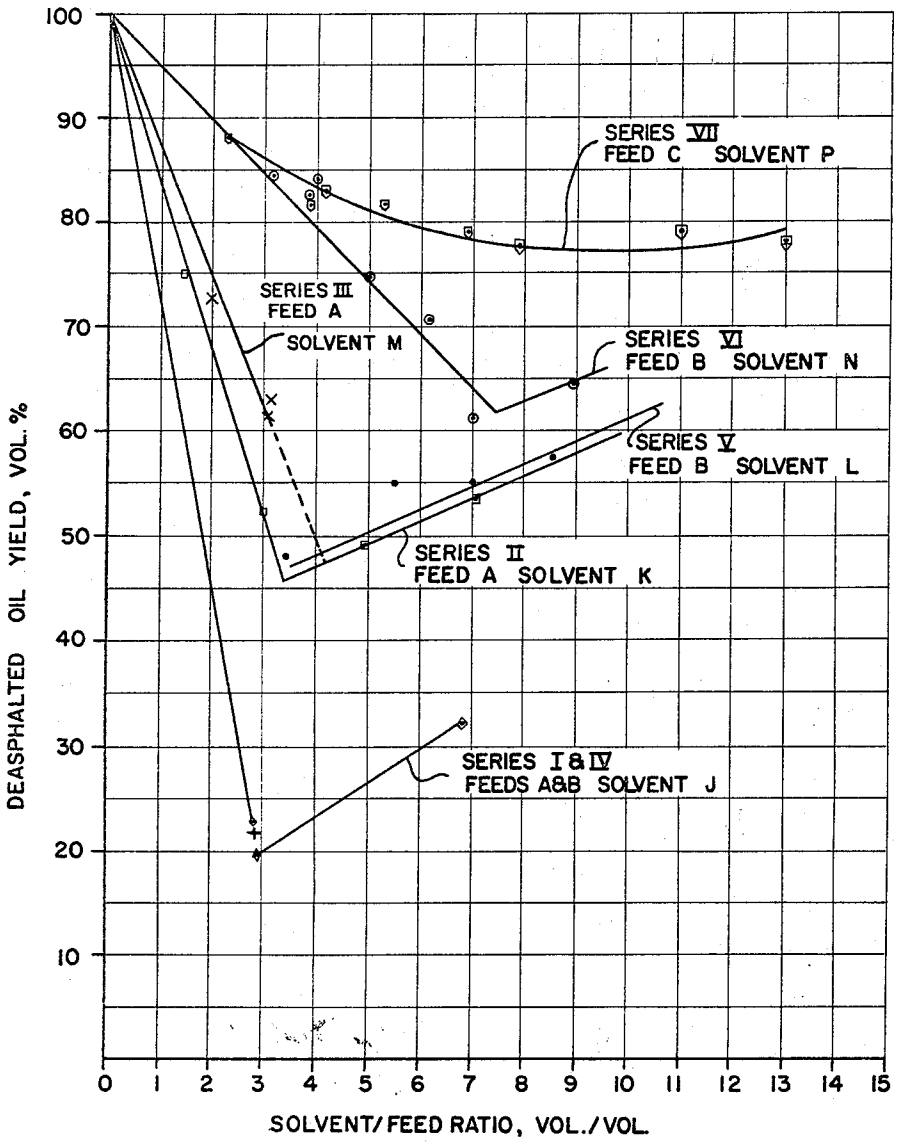
April 23, 1968 B. VALLINO, JR 3,379,639

RESIDUAL DEASPHALTING AND CRACKING WITH CATALYST DEMETALLIZATION

Filed Oct. 9, 1964 3 Sheets-Sheet 1

Fig 1



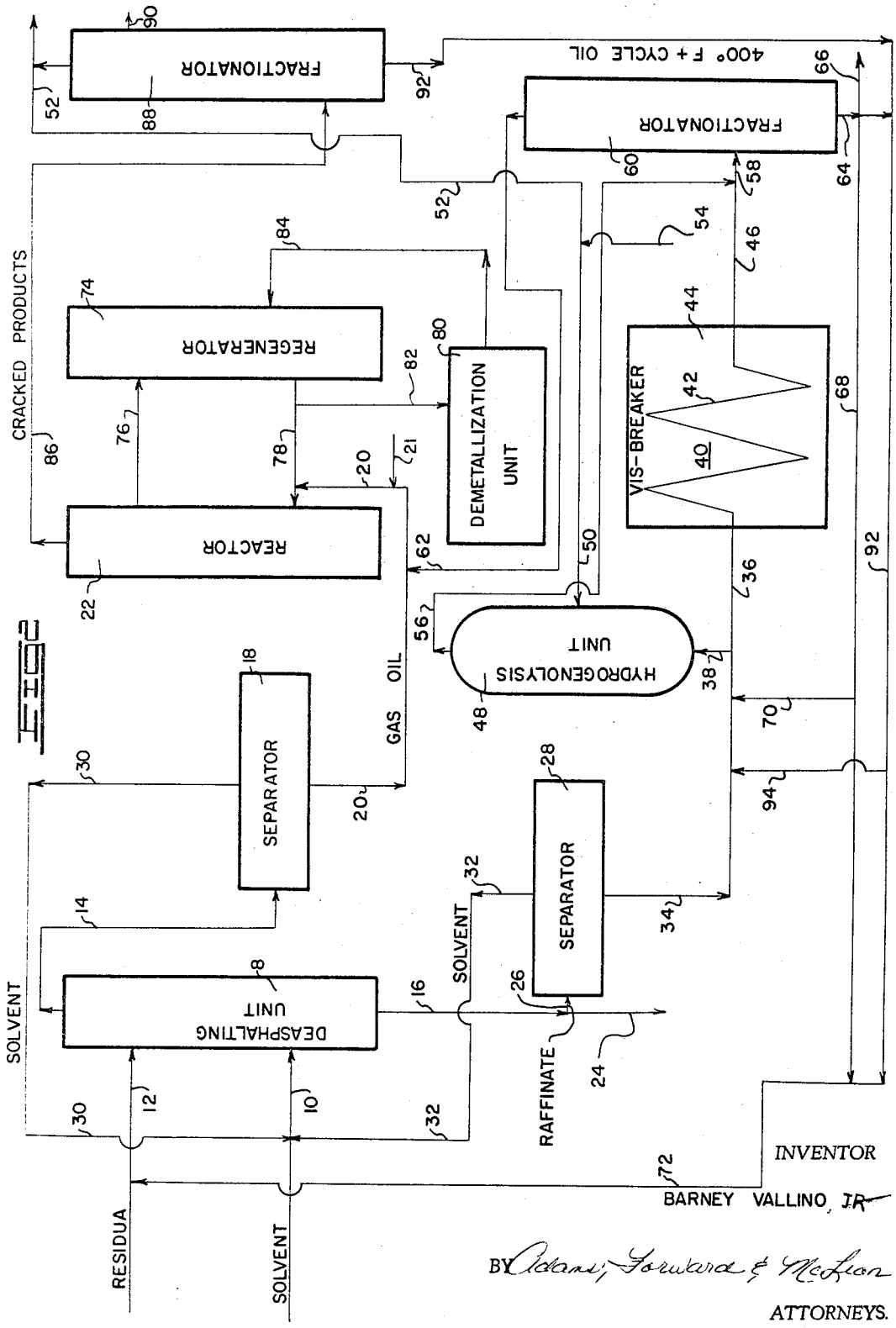
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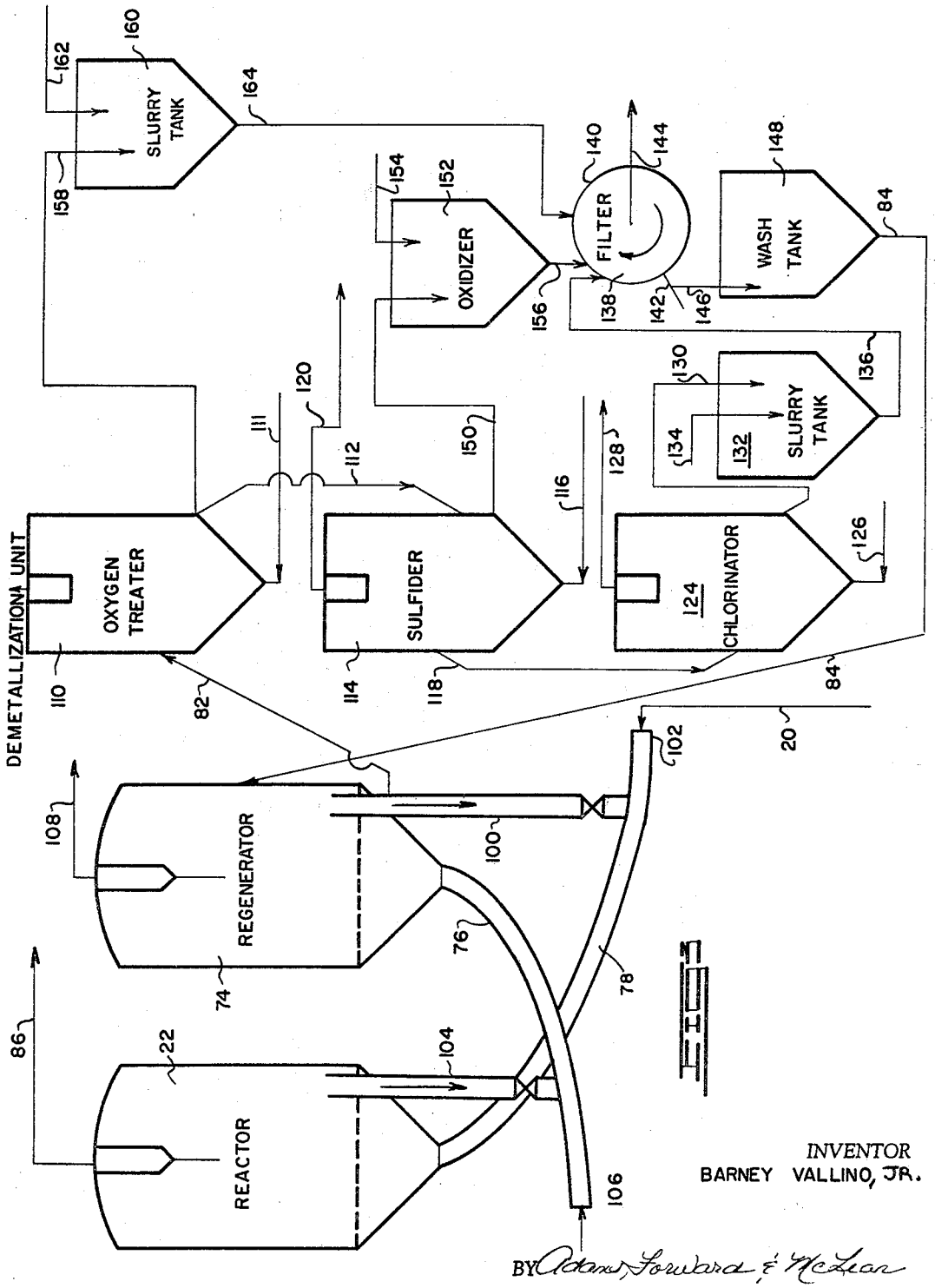
Filed Oct. 9, 1964 3 Sheets-Sheet 2



April 23, 1968 B. VALLINO, JR 3,379,639

RESIDUAL DEASPHALTING AND CRACKING WITH CATALYST DEMETALLIZATION

Filed Oct. 9, 1964 3 Sheets-Sheet 3



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3,379,639

RESIDUAL DEASPHALTING AND CRACKING WITH CATALYST DEMETALLIZATION

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Continuation-in-part of application Ser. No. 101,955, Apr. 10, 1961. This application Oct. 9, 1964, Ser. No. 402,968

11 Claims. (Cl. 208—80)

This is a continuation-in-part of my copending application S.N. 101,955, filed Apr. 10, 1961.

This invention relates to a hydrocarbon conversion process for obtaining increased yields of gasoline from a higher boiling residual petroleum hydrocarbon feed. Particularly, the process of this invention produces increased yields of gasoline by cracking gas oils, recovered from the residuum by solvent extraction, which are too highly contaminated with metals for conventional cracking operations. In one embodiment the extraction step of the invention produces high yields of gas oil from the residuum by carefully controlling the solvent-to-oil ratio in this step. The gas oil so recovered is high in metals content, but is suitable for cracking in the process of this invention when employing demetallizing techniques, hereinafter described, on the cracking catalyst to remove the poisoning metals. Thus, catalytic activity and selectivity are maintained.

Catalytically promoted cracking of heavier hydrocarbon feedstocks to produce hydrocarbons of preferred octane rating boiling in the gasoline range is widely practiced and uses a variety of solid oxide catalysts to give end products of fairly uniform composition. Cracking is ordinarily effected to produce gasoline as the most valuable product and is generally conducted at temperatures of about 750 to 1100° F., preferably about 850 to 950° F., at pressures up to about 200 p.s.i.g., preferably about atmospheric to 100 p.s.i.g., and without substantial addition of free hydrogen to the system. In cracking, the feedstock is usually a mineral oil or petroleum hydrocarbon fraction such as straight run or recycle gas oils or other normally liquid hydrocarbons boiling above the gasoline range. As is well known to those familiar with the art, gas oil is a broad, general term that covers a variety of stocks. The term, for instance, includes any fraction distilled from petroleum which has an initial boiling point of at least about 400° F. and an end boiling point of at least about 600° F., and boiling over a range of at least about 100° F. The portion which is not distilled is considered residual stock. The exact boiling range of a gas oil, therefore, will be determined by the initial distillation temperature (initial boiling point) and by the temperature at which distillation is cut off (end boiling point). In practice, petroleum distillations have been made under vacuum up to temperatures as high as about 1100–1200° F. (corrected to atmospheric pressure). Accordingly, in the broad sense, a gas oil is a petroleum fraction which boils essentially between two temperatures that establish a range falling within from about 400° F. to about 1100–1200° F. Thus, a gas oil could boil over the entire range 400–1200° F. or it could boil over a narrower range, e.g. 500–900° F.

A gas oil can be further roughly classified by boiling ranges. Thus, gas oil boiling between about 400° F. and about 600–650° F. is termed a light gas oil; a medium gas oil distills between about 600–650° F. and about 800–900° F.; a gas oil boiling between about 800–850° F. and about 1100–1200° F. is sometimes designated as a vacuum gas oil. It must be understood, however, that a particular stock may bridge two boiling ranges, or even span

several ranges, i.e. include, for example, light and medium gas oils.

A residual stock is in general the petroleum fractions higher boiling than gas oils and which are undistilled. Any fraction, regardless of its initial boiling point, which includes heavy bottoms, such as tars, asphalts, etc., may be termed a residual fraction. Accordingly, a residual stock can be the portion of the crude boiling above about 1100–1200° F., or it can be made up of a gas oil fraction plus the portion boiling above about 1100–1200° F. For instance, a topped crude may be the entire portion of the crude remaining after the light ends (the portion boiling up to about 400° F.) have been removed by distillation. Therefore, such a fraction includes the entire gas oil fraction (400° F. to 1100–1200° F.) and the undistilled portion of the crude petroleum boiling above about 1100–1200° F.

In recent times, a great deal of effort has been applied in petroleum refining to increase recovery of catalytic cracking feedstock of "gas oils" from residual fractions of petroleum oil, but attempts to employ heavier fractions of crude oil for catalytic cracking have been limited heretofore due to the presence of certain metal contaminants in such heavy fractions; the highest boiling fractions of many crude oils contain substantial portions of metal contaminants, particularly nickel and vanadium components perhaps present in quantities of about 10 to 50 pounds of metal per 1000 barrels of crude. Most of these metals, when present in a stock, deposit in a relatively non-volatile form on the catalyst during the conversion processes so that regeneration of the catalyst to remove coke does not remove these contaminants. Although referred to as "metals," these catalyst contaminants may be in the form of free metals or relatively non-volatile metal compounds. It is to be understood that the term "metal" used herein refers to either form.

Catalytic cracking operations are adversely affected by the presence of metal contaminants such as nickel and vanadium which continue to accumulate on the catalyst and alter the catalytic properties of the catalyst. One of the effects of such catalyst poisoning is to cause excessive hydrogen and coke to be produced during catalytic cracking, with a loss in hydrocarbon product. In some actual commercial operations hydrogen production has become so severe, due to catalyst poisoning, as to cause failure of gas compressors due to the change in the density of the gases, resulting in flooding of light end fractionating equipment and the like. It is to be understood, therefore, that the problem of catalyst contamination prevents full exploitation of metal contaminated feed. Charge stocks containing more than about 1.5 part per million of vanadium and/or 0.6 part per million of nickel are generally avoided in catalytic cracking and most refiners prefer less than about 0.5 part per million of vanadium or less than about 0.2 part per million of nickel in a cracking stock. In this regard, see the discussion on page 126 of "Petroleum Refiner." vol. 32, No. 2, February 1953.

One technique adopted in the art for preventing catalyst contamination is a selective solvent treatment for the residual to remove gas oil, while leaving behind a heavy fraction containing most of the metal contaminants which are normally present. The solvent extraction process (deasphalting) comprises contacting a residual petroleum fraction containing a major portion of components boiling above about 900° F. with a hydrocarbon solvent under conditions to form a gas oil extract phase substantially free from metal contaminants, and an asphalt raffinate phase, containing substantially all of the metal contaminants of the feedstock. This raffinate phase is generally not employed in gasoline production because of its high metal content but rather is diverted to low-value uses, such as low-grade fuel or road surfacing materials.

Ordinarily solvent treatment leaves a good portion of the gas oil components in the raffinate phase, since deeper cutting produces a gas oil too heavily contaminated with metals for ordinary cracking systems. Also, solvent extraction may often require an amount of solvent considered to be prohibitive when a substantially metals-free cracking feedstock is to be produced.

It is an object of the present invention to provide an integrated process for the treatment of residual fractions such as asphaltic gas oils or reduced asphaltic crudes containing metal contaminants, in which the steps of solvent extraction, catalytic cracking and catalyst demetallization are combined and adjusted to minimize the yield of low value products and to maximize the yields of high quality products such as high octane gasoline and other valuable constituents. The residual oil ordinarily will not require a conversion step, such as hydrogen treating or visbreaking before the solvent extraction step.

The feeds to the present process comprise petroleum residua which may be exemplified by vacuum residua, atmospheric residua, tars, pitches, etc., boiling primarily above about 600° F. or even above about 900° F. The residual feed often has an API gravity in the range of about 0° to 25°, a Conradson carbon content in the range of about 3 to 35 weight percent and a viscosity often above about 200 seconds Saybolt Furol at 210° F. These charge stocks contain metals which are poisonous to the cracking catalyst to be used subsequently. The process of this invention, with its demetallization features, is economically attractive for residual feedstocks containing as little as about 5 or 15 p.p.m. nickel, and/or about 10 or 25 p.p.m. vanadium. The residual feedstock will usually include at least about 5 or 10 parts per million of one or more of vanadium and nickel. These are materials generally avoided for use as cracking feeds. In the process of this invention metal contents above these ranges may be present; it will be apparent that oils having metal contents in these generally undesirable ranges are the oils which this invention salvages. A mixture of vanadium and nickel may be considered as harmful as a single metal even though the individual amounts of each metal are below the values mentioned above because the effect of the total amount of the metallic components is frequently sufficient to give harmful effects during catalytic cracking. In most cases, however, the total of one or both of these metals in the residual will be at least about 5 p.p.m. The maximum amount of metals in the residuals can vary widely; preferably the maximum amount of these poisoning metals in the residual stock will not exceed about 50 p.p.m. nickel, about 100 p.p.m. vanadium. Feeds containing as much as about 250 p.p.m. nickel, and 500 or 1000 p.p.m. vanadium or more may be processed by this invention but economic factors may be adversely affected at these high levels.

The prior art has proposed use of hydrocarbon solvents for recovery of gas oils from residuals, but generally the solvent-to-oil ratios are high. The amount of gas oil component recoverable from residuals by any particular solvent varies with the volume ratio of solvent to residual used in the extraction; for each solvent a certain ratio exists where gas oil recovery is at a minimum, (Minimum Recovery Ratio). When a greater solvent-to-oil ratio is employed, a greater amount of gas oil having a low metals content is obtained. In one embodiment, the present invention exploits the discovery that even higher yields of gas oil are obtainable from residuals by extraction with low boiling hydrocarbons at a solvent-to-oil ratio *less* than that at which the minimum yield is obtained for the given feed, solvent and operating conditions. Besides the higher yields of gasoline therefore ultimately obtainable for a given amount of residuum, this invention requires less solvent to be used. Experimental work with a variety of hydrocarbon solvents has yielded data which show the effect of various operating ratios on the amount of gas oil extractable from various residual fractions. The results

of this work are given in Table II below and in FIGURE 1 of the drawings. The residuals fractions employed, termed A, B and C, were asphalt fractions of a mixed Mid-Continent crude having an initial boiling point of at least about 400° F. at atmospheric pressure. The characteristics of the feedstocks subjected to solvent extraction are reported in Table I.

TABLE I

	A	B	C
Specific Gravity 60/60° F	0.995	0.995	0.9944
Specific Gravity 77/77° F	0.988	0.988	0.9937
Penetration at 77° F	234	262	179
Carbon Residue (Conradson), Wt. percent	19.72	17.78	17.03-19.6
Viscosity:			
FV/21° F	600.5	569	814
FV/275° F	90.4	89.2	105.6
Ring and Ball Softening Point, ° F	100	100	115
Molecular Wt	1,146-1,160	1,149	1,180
Hydrogen, Wt. percent	10.81-10.86	10.46	10.70
Pentane Insolubles	13.98	12.79	15.40
Benzene Insolubles	1.33	2.44	1.25
Sulfur, Wt. percent	1.00	0.98	0.98
NiO, p.p.m.	76.8-77.5	57.76	85
V_2O_5, p.p.m.	122.0-126	94.50	165

These feedstocks were contacted countercurrently with liquid hydrocarbon solvents as follows:

TABLE II

Series	I	II	III	IV	V	VI	VII
Feed	A	A	A	B	B	B	C
Solvent:							
Designation	J	K	M	J	L	N	P
Composition (approx.), percent:							
Propane	100	85	62	100	76		
Butane		15	38		24	100	80
Pentane							20
Extractor:							
Temp. (° F.)	150	150	150	150	150	260	230
Pressure (p.s.i.g.)	450	650	400	450	500	450	400

Table III shows the yield and characteristics of a deasphalted gas oil (DAGO) obtained from feed A with solvent K (series II) at various solvent-to-oil ratios.

TABLE III

Run No.	Vol. Ratio Solvent to Feed	Yield DAGO, Vol. percent	Pentane Insolubles, Wt. percent	DAGO Inspections		
				Conradson Carbon	NiO, p.p.m.	V_2O_5, p.p.m.
(1)	3.0	52.0	0.32	5.7	9	9
(2)	7.1	53.3	0.48	3.8	2.2	1.9
(3)	4.9	49.4	0.42	4.2	3.4	2.0
(4)	1.4	75.1	4.7	13.4	32.4	73.7

Yield results of series I through VII are given in FIGURE 1 of the drawings. It will clearly be seen from the drawing that high yields of DAGO are obtained from asphalt residua by reducing the solvent-to-oil ratio below the minimum recovery ratio. Also, it will be observed from the curves of FIGURE 1 that these yields are in many cases even higher than are obtainable using the higher ratios of solvent-to-oil favored by the art. Also, as seen from Table III, the DAGO produced at low solvent-to-oil ratios has a progressively increasing content of the poisoning metals nickel and vanadium.

This invention provides for use of improved extraction techniques with the resultant high metal content gas oil being catalytically cracked and the amount of catalyst poisoning being controlled by the use of demetallization procedures, that is, procedures for removing a significant amount of poisoning metal from the catalyst. The solvent-to-oil ratio is adjusted to provide an extract containing at least about 1.5 p.p.m. nickel, measured as the oxide, and/or 2.0 p.p.m. vanadium, measured as the pentoxide, in order to justify the provisions made for cracking catalyst demetallization.

The hydrocarbon solvent usually contains from about 3 to about 7 carbon atoms and preferably about 3 to 5 carbon atoms. Specific hydrocarbons which may be used in the liquid form as solvents are propane, propylene, butylene, butane, including iso- and normal butane, pentane, etc., or any combination thereof. For example, a hydrocarbon mixture containing 5–90% butane, and preferably about 10–50% butane may be used with advantage. After contacting, the mixture of residual and solvent separates into two phases, and extract phase containing solvent and gas oil components and a raffinate or asphalt phase. The two phases are separately withdrawn, the hydrocarbon is removed from the extract phase as desired, and the deasphalted gas oil is then used as a feedstock to a catalytic cracking operation.

The amount of the hydrocarbon employed in this invention may be within the range of about 1 to about 10 volumes of the solvent per volumn of residual petroleum fraction employed as a feedstock to the deasphalting zone, and preferably the solvent-to-oil ratio is less than that at which the minimum yield of gas oil is obtained for the given feed, solvent and operating conditions. The minimum recovery ratio may vary with different feedstocks as shown above. The most preferred range of a propane-butane mixture may be about 3 to 7 volumes of the solvent per volume of residual oil.

The solvent extraction deasphalting step may be conducted within a wide range of temperatures. The minimum will be the softening point of the asphalt feed, while the maximum will be the boiling temperature of the solvent at the pressure used. The extraction step will frequently be performed at a temperature of about 100 to 300° F. There may be a temperature gradient in the deasphalting step with the highest temperature found at the deasphalted oil (extract phase) outlet. The temperature gradient may be within the range of about 0° to 60° F. Preferably about a 20–45° F. temperature gradient should be maintained, for example a 30° gradient may be used where the top of the tower is the point where the deasphalted oil is withdrawn. Thus, the temperature at the top of the extraction tower may be maintained at 180° F. while the bottom of the tower, where the asphalt is removed, may be at about 150° F. Normal operating pressures should be higher than the vapor pressure of the solvent system used at the temperature of operation. For example, in a solvent system comprising propane-butane mixtures, pressure within the range of about 400–700 p.s.i.g. may be used. The invention may be carried out in a plurality of stages in one vessel or in a plurality of vessels in series. The separate stages may be conducted with a temperature gradient and pressure gradient between the stages.

The solvent extraction step of the process of this invention as pointed out above, removes from the residual treated a good yield of gas oil components as an extract phase. This phase is conducted to a zone where, for example, by a pressure and/or temperature change the solvent hydrocarbons are vaporized leaving a liquid deasphalted gas oil product suitable for use in this invention as a catalytic cracking feedstock. The deoiled asphalt raffinate phase may also be used to provide further gas oil components for the cracking feedstock. Such gas oil components may be supplied by converting components of the deoiled asphalt into materials suitable for use as part of the cracker feed, for example, by reducing the carbon chain length of some asphalt fraction components as by visbreaking and/or by increasing the hydrogen-to-carbon ratio of some of these components, for instance, by hydrotreating. These operations are performed preferably after removal of solvent entrained in the raffinate by any convenient means such as by volatilizing the traces of solvent, washing them out with water or disentraining solvent by the use of steam.

The carbon chain length of some asphalt fraction components may be shortened by subjecting the deoiled asphalt to a mild thermal cracking or visbreaking treatment. In the visbreaker, relatively high temperatures and short contact times may be employed. Temperatures in the range of about 800–950° F. at the visbreaker outlet may be employed. The effluent is fractionated and the bottoms may be recycled to the extraction step where it may be further treated, for example, with extracting solvents, or it may be drawn off from the system and used as a low value fuel oil. The gas oil formed in the visbreaking operation may be combined with the gas oil from the solvent extractor and passed to the catalytic reactor.

Alternatively, the deoiled asphalt product from the extraction step may be hydrogenated to improve the hydrogen-to-carbon ratio. Some cracking may also occur in this treatment. The hydrogenolysis step may be carried out over a catalyst, preferably a sulfide or oxide of molybdenum or tungsten, which is resistant to poisoning by sulfur. Suitable operating conditions are: a temperature in the range of 750–900° F., a pressure in the range of 300–3000 p.s.i.g. and a liquid space velocity of 0.5 to 2.5 volumes of charge oil per volume of catalyst per hour. Hydrogen is provided from any convenient source and consumption is in the range of about 2000 to 3000 cubic feet per barrel of charge. The effluent from the hydrogenolysis unit is separated by fractionation into a gas oil fraction which may be combined with the gas oil from the solvent extraction and passed to the cracker. The residue of the hydrogenolysis, for instance, boiling above about 550° F., may be removed from the system, or as an alternative, may be passed back to the deasphalting unit or recycled to the hydrogenolysis unit.

Hydrotreating gives a partial reduction in metals content of the cracking feed. The metals remaining in the hydrocarbon oils accumulate on the cracking catalyst during the cracking operation and unless steps are taken to prevent excess accumulation, excessive dehydrogenation takes place in the cracking, partially undoing the work performed in the hydrotreating step and severely reducing the yield of gasoline in the cracker effluent. Hydrotreating may remove only about 10% of the poisoning metal in the hydrotreater feed, but preferably much more of the poison. Thus the hydrotreated product used in cracking contains perhaps about 50 to 90 or more weight percent less of one or both of nickel and vanadium than the hydrocarbon charged to the hydrotreating reaction; preferably there is this much reduction in nickel and vanadium or in each of these metals. Frequently the reduction of one or all of nickel, vanadium and iron will be about 65 to 90 weight percent. The conditions of hydrotreating are adjusted to give the desired amount of metals removal. This amount, in turn, is determined by a number of factors: the amount of poison remaining in the hydrotreated product, the proportion of hydrotreated product sent to the catalytic cracking, the amount of other hydrocarbon material with which the hydrotreater effluent is blended to prepare the cracker feed, and the poisoning metal content of this additional feedstock.

The recovered gas oil is subjected to catalytic cracking. Contaminating metals in greater quantities than are acceptable to the art generally are present in the cracker feedstock. The cracking feedstock boils above the gasoline range, preferably in the range of about 600–1100° F. and contains a significant amount of the solvent treatment product. The amount of this product in the cracking feed will be at least about 5–10%, preferably about 20–70%. The product may comprise gas oil fractions from the extract phase of the solvent treatment or from the visbroken or hydrotreated raffinate or both. The remaining portion of cracker feed may comprise cracking feeds of more or less conventional types, that is, virgin gas oil fractions or recycle gas oils from this cracker or other catalytic crackers, etc. The deasphalting and hydrotreating or visbreaking conditions and the proportion of gas oil included in the cracker feed will be adjusted to provide a feed containing more than about 0.3 p.p.m. nickel and/or 0.5 p.p.m. vanadium in order to justify the provisions made in

this invention for cracking catalyst demetallization and preferably the total feed to cracking will contain more than about 1 p.p.m. nickel and about 2 p.p.m. vanadium but less than about 30 p.p.m. nickel and/or 60 p.p.m. vanadium.

Catalytic cracking is ordinarily effected to produce gasoline as the most valuable produce and is generally conducted at temperatures of about 750 to 1050° F., preferably about 850 to 975° F., at pressures up to about 100 p.s.i.g., preferably about atmospheric to 5 to 15 p.s.i.g., and advantageously without substantial addition of free hydrogen to the system. In the cracking operation as in the hydrotreating, a batch, semi-continuous or continuous system may be used but most often is a continuous fluidized system.

The cracking catalyst is of the solid refractory metal oxide type known in the art, for instance silica, alumina, magnesia, titania, etc., or their mixtures. Of most importance are the synthetic gel-containing catalysts, such as the synthetic and the semi-synthetic, i.e. synthetic gel supported on a carrier such as natural clay, cracking catalysts. The cracking catalysts which have received the widest acceptance today are usually predominantly silica, that is silica-based, and may contain solid acidic oxide promoters, e.g. alumina, magnesia, etc., with the promoters usually being less than about 35% of the catalyst, preferably about 5 to 25%. These compositions are calcined to a state of very slight hydration. The cracking catalyst can be of macrosize, for instance, bead form or finely divided form, and employed as a fixed, moving or fluidized bed as noted with respect to the hydrotreating catalyst. In a highly preferred form of this invention finely divided (fluid) catalyst, for instance having particles predominantly in the 20 to 150 micron range, is disposed as a fluidized bed in the reaction zone to which the feed is charged continuously and is reacted essentially in the vapor phase.

Vaporous products are taken overhead and a portion of the catalyst is continuously withdrawn and passed to a regeneration zone where coke or carbon is burned from the catalyst in a fluidized bed by contact with a free oxygen-containing gas before its return to the reaction zone. In a typical opertaion the catalytic cracking of the hydrocarbon feed would normally result in the conversion of about 40 to 70%, preferably about 50 to 60%, of the feedstock into a product boiling in the gasoline range. The effluent from the cracker conveniently is distilled to isolate the gasoline fraction. Also, products, such as fixed gases, boiling below the gasoline range are removed from the system. Bottoms, that is, products boiling above the gasoline range conveniently are recycled to the deasphalting zone, hydrotreating unit or visbreaker or to the catalytic cracking zone by blending them with virgin feed and/or the deasphalted gas oil extract. These bottoms, or cycle oil, are substantially free of metal poisons.

In cracking, coke yield may be held to a minimum through the use of good steam stripping and a high steam partial pressure, and removal of coke from the catalyst is performed by regeneration. Regeneration of a catalyst to remove carbon is a relatively quick procedure in most commercial catalytic conversion operations. For example, in a typical fluidized cracking unit, a portion of catalyst is continually being removed from the reactor and sent to the regenerator for contact with air at about 950 to 1200° F., more usually about 1000 to 1150° F. Combustion of coke from the catalyst is rapid, and for reasons of economy only enough air is used to supply the needed oxygen. Average residence time for a portion of catalyst in the regenerator may be on the order of about six minutes and the oxygen content of the effluent gases from the regenerator is desirably less than about ½%. The regeneration of any particular quantum of catalyst is generally regulated to give a carbon content of less than about 5.0%, generally less than about 0.5%. Regeneration puts the catalyst in a substantially carbon-free state, that is, the state where little, if any, carbon is burned or oxygen consumed even when the catalyst is contacted with oxygen at temperaures conducive to combustion.

In the treatment to take poisoning metals from the cracking catalyst the amount of metal is removed which is necessary to keep the average metal content of the catalyst in the cracking system below the limit of the unit's tolerance for poison. The tolerance of the cracker for poison in turn determines to a large extent the amount of metals removed in the catalyst demetallization procedure. Where the catalyst contains a greater amount of poisoning metal, a particular treatment will remove a greater amount of metal, for example, if the cracker can tolerate an average of 100 p.p.m. Ni and the demetallization process can remove 50% of the nickel content of the catalyst, only 50 p.p.m. of nickel can be removed in a pass through the catalyst demetallization system. However, where the cracker can tolerate 500 p.p.m. of nickel, it is possible to remove 250 p.p.m. nickel from the catalyst with each pass through the demetallization system. It is advisable, therefore, to operate the cracking and demetallization procedures with a catalyst having a metals content near the limit or tolerance of the cracker for poisoning metals. This tolerance for poisoning metal oxide is seldom greater than about 5000–10,000 p.p.m. Catalyst demetallization is not economically justified unless the catalyst contains at least about 50 p.p.m. nickel and/or 50 p.p.m. vanadium. Preferably the equilibrium metals level is allowed to exceed about 200 p.p.m. nickel and/or 500 p.p.m. vanadium so that the total metals removal will be greater per pass through the demetallizer.

In the treatment to take poisoning metals from the cracking catalyst a large or small amount of metal can be removed as desired. The demetallization treatment generally removes about 10 to 90% of one or more poisoning metals from a catalyst portion which passes through the treatment. Preferably a demetallization system is used which removes about 60 to 90% nickel and 20 to 40% vanadium from the treated portion of catalyst. Preferably at least 50% of the equilibrium nickel content and 15% of the equilibrium vanadium content is removed. The actual time or extent of treating depends on various factors, and is controlled by the operator according to the situation he faces, e.g. the extent of metals content in the feed, the level of conversion unit tolerance for poison, the sensitivity of the particular catalyst toward a particular phase of the demetallization procedure, etc. Also, the thoroughness of treatment of any quantum of catalyst in commercial practice is balanced against the demetallization rate chosen; that is, the amount of catalyst, as compared to the total catalyst in the conversion system proper, which is subjected to the demetallization treatment per unit of time. A high rate of catalyst withdrawal from the conversion system and quick passage through a mild demetallization procedure may suffice as readily as a more intensive demetallization at a slower rate to keep the total of poisoning metal in the conversion reactor within the tolerance of the unit for poison. In a continuous operation of the commercial type a satisfactory treating rate may be about 5 to 50% of the total catalyst inventory in the system, per twenty four hour day of operation although other treating rates may be used. With a continuously circulating catalyst stream, such as in the ordinary "fluid" system a slip-stream of catalyst, at the "equilibrium" level of poisoning metals may be removed intermittently or continuously from the regenerator standpipe of the cracking system. The catalyst is subjected to one or more of the demetallization procedures described hereinafter and then the catalyst, substantially reduced in contaminating metal content, is returned to the cracking system.

The demetallization of the catalyst will generally include one or more processing steps. U.S. Patents Nos. 3,122,497, 3,122,510, 3,122,511, 3,122,512, 3,147,209, 3,147,228 and copending patent applications Ser. Nos. 758,681, now abandoned, filed Sept. 3, 1958; 39,810, now Patent No. 3,168,481, filed June 30, 1960; 47,598, now

Patent No. 3,168,482, filed Aug. 4, 1960; 53,623, now abandoned, filed Sept. 2, 1960; 55,160 now Patent No. 3,150,103, and 55,184, now abandoned, filed Sept. 12, 1960; 67,518, now Patent No. 3,208,952, filed Nov. 7, 1960; 73,199, now Patent No. 3,131,088, filed Dec. 2, 1960, and 264,709, now abandoned, filed Mar. 12, 1963, all of which are hereby incorporated by reference, describe procedures by which vanadium and other poisoning metals included in a solid oxide hydrocarbon conversion catalyst are removed by dissolving them from the catalyst or subjecting the catalyst, outside the hydrocarbon conversion system, to elevated temperature conditions which put the metal contaminants into the chloride, sulfate or other volatile, water-dispersible or more available form. A significant advantage of these processes lies in the fact that the overall metals removal operation, even if repeated, does not unduly deleteriously affect the activity, selectivity, pore structure and other desirable characteristics of the catalyst.

As mentioned, the processing procedure of this invention incorporates several processing improvements which make it considerably more attractive to catalytically crack metal contaminated gas oil extracted from residual oils. The deleterious effects of catalyst deactivating metal compounds are overcome to a great extent by combining solvent extraction with one or more of the demetallization processes described hereinafter. This permits extracting and cracking a greater percentage of metal contaminated gas oils without discarding large amounts of expensive cracking catalyst in order to keep catalyst metal level low.

Treatment of the regenerated catalyst with molecular oxygen-containing gas is employed to improve the removal of vanadium from the poisoned catalyst. This treatment is described in copending application Ser. No. 55,160, and is preferably performed at a temperature at least about 50° F. higher than the regeneration temperature, that is, the average temperature at which the major portion of carbon is removed from the catalyst. The temperature of treatment with molecular oxygen-containing gas will generally be in the range of about 1000 to 1800° F. but below a temperature where the catalyst undergoes any substantial deleterious change in its physical or chemical characteristics, preferably a temperature of about 1150 to 1350° or even as high as 1600° F. The duration of the oxygen treatment and the amount of vanadium prepared by the treatment for subsequent removal is dependent upon the temperature and the characteristics of the equipment used. If any significant amount of carbon is present in the catalyst at the start of this high-temperature treatment, the essential oxygen contact is that continued after carbon removal, which may vary from the short time necessary to produce an observable effect in the later treatment, say, a quarter of an hour to a time just long enough not to damage the catalyst. In any event, after carbon removal, the oxygen treatment of the essentially carbon-free catalyst is at least long enough to stabilize a substantial amount of vanadium in its highest valence state, as evidenced by a significant increase, say at least about 10%, preferably at least about 100%, in the vanadium removal in subsequent stages of the process. This increase is over and above that which would have been obtained by the other metals removal steps without the oxygen treatment. The maximum practical time of treatment will vary from about 4 to 24 hours, depending on the type of equipment used. The oxygen-containing gas used in the treatment contains molecular oxygen as the essential active ingredient and there is little significant consumption of oxygen in the treatment. The gas may be oxygen, or a mixture of oxygen with inert gas, such as air or oxygen-enriched air, containing at least about 1%, preferably at least about 10% O_2. The partial pressure of oxygen in the treating gas may range widely, for example, from about 0.1 to 30 atmospheres, but usually the total gas pressure will not exceed about 25 atmospheres.

The catalyst may pass directly from the oxygen treatment to a vanadium removal treatment especially where this is the only important contaminant, as may be the case when a feed is derived, for example, from Venezuelan crude. Such treatment may be a basic aqueous wash such as described in copending application Ser. No. 39,810. Alternatively, vanadium may be removed by a chlorination procedure as described in U.S. Patent No. 3,122,510.

Vanadium may be removed from the catalyst after the high temperature treatment with molecular oxygen-containing gas by washing it with a basic aqueous solution. The pH is frequently greater than about 7.5 and preferably the solution contains ammonium ions which may be NH_4+ ions or organic-substituted NH_4+ ions suc has methyl ammonium and quaternary hydrocarbon radical ammoniums. The amount of ammonium ion in the solution is suffifficient to give the desired vanadium removal and will often be in the range of about 1 to 25 or more pounds per ton of catalyst treated. The temperature of the wash solution may vary within wide limits: room temperature or below, or higher. Temperatures above 215° F. require pressurized equipment, the cost of which does not appear to be justified. Very short contact times, for example, about a minute, are satisfactory, while the time of washing may last 2 to 5 hours or longer. After the ammonium wash the catalyst slurry can be filtered to give a cake which may be reslurried with water or rinsed in other ways, such as, for example, by a water wash on the filter, and the rinsing may be repeated, if desired, several times.

Alternatively, after the high temperature treatment with oxygen-containing gas, treatment of a metals contaminated catalyst with a chlorinating agent at a moderately elevated temperature up to about 1000° F. is of value in removing vanadium from the catalyst as volatile chlorides. This treatment is described in Patient 3,122,510. The chlorination takes place at a temperature of at least about 300° F., preferably about 550 to 650° F. with optimum results usually being obtained near 600° F. The chlorinating agent is essentially anhydrous, that is, if changed to the liquid state no separate aqueous phase would be observed in the reagent.

The chlorinating reagent is a vapor which contains chlorine or sometime HCl, preferably in combination with carbon or sulfur. Such reagents include molecular chlorine but preferably are mixtures of chlorine with, for example, a chlorine substituted light hydrocarbon, such as carbon tetrachloride, which may be used as such or formed in-situ by the use of, for example, a vaporous mixture of chlorine gas with low molecular weight hydrocarbons such as methane, n-pentane, etc. About 1 to 40% active chlorinating agent based on the weight of the catalyst is generally used. The carbon or sulfur compound promoter is generally used in the amount of about 1 to 5 or 10% or more, preferably about 2 to 3%, based on the weight of the catalyst for good metals removal; however, even if less than this amount is used, a considerable improvement in metals conversion is obtained over that which is possible at the same temperature using chlorine alone. The chlorine and promoter may be supplied individually or as a mixture to a poisoned catalyst. Such a a mixture may contain about 0.1 to 50 parts chlorine per part of promoter, preferably about 1 to 10 parts per part of promoter. A chlorinating gas comprising about 1 to 30 weight percent chlorine, based on the catalyst, together with 1% or more S_2Cl_2 gives good results. Preferably, such as gas provides 1 to 10% Cl_2 and about 1.5% S_2Cl_2, based on the catalyst. A "saturated" mixture of CCl_4 and Cl_2 or HCl can be made by bubbling chlorine or hydrogen chloride gas at room temperature through a vessel containing CCl_4; such a mixture generally contains about 1 part CCl_4:5 to 10 parts Cl_2 or HCl. Conveniently, a

pressure of about 0 to 100 or more p.s.i.g., preferably about 0 to 15 p.s.i.g., may be maintained in chlorination. The chlorination may take about 5 to 120 minutes, more usually about 20 to 60 minutes, but shorter or longer reaction periods may be possible or needed, for instance, depending on the linear velocity of the chlorinating and purging vapors.

The demetallization procedure employed in this invention may be directed toward nickel removal from the catalyst, generally in conjunction with vanadium removal. Nickel removal may be accomplished by dissolving nickel compounds directly from the catalyst and/or by converting the nickel compounds to volatile materials and/or materials soluble or dispersible in an aqueous medium, e.g. water or dilute acid. The water-dispersible form may be one which decomposes in water to produce water-soluble products. The removal procedure for the converted metal may be based on the form to which the metal is converted. The mechanism of the washing steps may be one of simultaneous conversion of nickel and/or vanadium to salt form and removal by the aqueous wash; however, this invention is not to be limited by such a theory.

Conversion of some of the metal poisons, especially nickel, to a water-dispersible form is described in co-pending application Ser. No. 264,709, by subjecting the catalyst to a sulfating gas, that is SO_2, SO_3 or a mixture of SO_2 and O_2, at an elevated temperature. Sulfur oxide contact is usually performed at a temperature of about 500 to 1200° F. and frequently it is advantageous to include some free oxygen in the treating gas. Another procedure, described in U.S. Patents 3,147,209 and 3,147,228, includes sulfiding the catalyst and performing an oxidation process, after which metal contaminants in water-dispersible form, preferably prior to an ammonium wash, may be removed from the catalyst by an aqueous medium.

The sulfiding step can be performed by contacting the poisoned catalyst with elemental sulfur vapors, or more conveniently by contacting the poisoned catalyst with a volatile sulfide, such as H_2S, CS_2 or a mercaptan. The contact with the sulfur-containing vapor can be performed at an elevated temperature generally in the range of about 500 to 1500° F., preferably about 800 to 1300° F. Other treating conditions can include a sulfur-containing vapor partial pressure of about 0.1 to 30 atmospheres or more, preferably about 0.5 to 25 atmospheres. Hydrogen sulfide is the preferred sulfiding agent. Pressures below atmospheric can be obtained either by using a partial vacuum or by diluting the vapor with gas such as nitrogen or hydrogen. The time of contact may vary on the basis of the temperature and pressure chosen and other factors such as the amount of metal to be removed. The sulfiding may run for, say up to about 20 hours or more depending on these conditions and the severity of the poisoning. Temperatures of about 900 to 1200° F. and pressures approximating 1 atmosphere or less seem near optimum for sulfiding and this treatment often continues for at least 1 or 2 hours but the time, of course, can depend upon the manner of contacting the catalyst and sulfiding agent and the nature of the treating system, e.g. batch or continuous, as well as the rate of diffusion within the catalyst matrix. The sulfiding step performs the function not only of supplying a sulfur-containing metal compound which may be easily converted to a water-dispersible form but also appears to concentrate some metal poisons, especially nickel, at the surface of the catalyst particle.

Oxidation after sulfiding may be performed by a gaseous oxidizing agent to provide metal poisons in a dispersible form. Gaseous oxygen, or mixtures of gaseous oxygen with inert gases such as nitrogen, may be brought into contact with the sulfided catalyst at an oxygen partial pressure of about 0.2 atmosphere and upward, temperatures upward of room temperature and usually not above about 1300° F., and times dependent on temperature and oxygen partial pressure. Gaseous oxidation is best carried out near 900° F., about one atmosphere O_2 and at very brief contact times.

The metal sulfide may be rendered water-dispersible by a liquid aqueous oxidizing agent such as a dilute hydrogen peroxide or hypochlorous acid water solution, as described in Patent 3,147,228. The inclusion in the liquid aqueous oxidizing solution of sulfuric acid or nitric acid has been found greatly to reduce the consumption of peroxide. In addition the inclusion of nitric acid in the oxidizing solution provides for increased vanadium removal. Useful proportions of acid to peroxide to catalyst generally include about 2 to 25 pounds acid (on a 100% basis) to about 1 to 30 pounds or more H_2O_2 (also on a 100% basis) in a very dilute aqueous solution, to about one ton of catalyst. A 30% H_2O_2 solution in water seems to be an advantageous raw material for preparing the aqueous oxidizing solution. Sodium peroxide or potassium peroxide may be used in place of hydrogen peroxide and in such circumstances extra sulfuric or nitric acid may be used.

Another highly advantageous oxidizing medium is an aerated dilute nitric acid solution in water. Such a solution may be provided by continuously bubbling air into a slurry of the catalyst in very dilute nitric acid. Other oxygen-containing gases may be substituted for air. Varying oxygen partial pressure in the range of about 0.2 to 1.0 atmosphere appears to have no effect in time required for oxidation, which is generally at least about 7 to 8 minutes. The oxidizing slurry may contain about 20% solids and provide about 5 pounds of nitric acid per ton of catalyst. Studies have shown a greater concentration of HNO_3 to be of no significant advantage. Other oxidizing agents, such as chromic acid where a small residual Cr_2O_3 content in the catalyst is not significant, and similar aqueous oxidizing solutions such as water solutions of manganates and permanganates, chlorites, chlorates and perchlorates, bromites, bromates and perbromates, iodites, iodates and periodates, are also useful. Bromine or iodine water, or aerated, ozonated or oxygenated water, with or without acid, also will provide a dispersible form. The liquid phase oxidation may also be performed by exposing the sulfided catalyst first to air and then to the aqueous nitric acid solution. The conditions of oxidation can be selected as desired. The temperature can conveniently range up to about 220° F. with temperatures of above about 150° F. being preferred. Temperatures above about 220° F. necessitate the use of superatmospheric pressures and no need for such has been found.

After conversion of nickel sulfide to a dispersible form, the catalyst is washed with an aqueous medium to remove the metal poisons. This aqueous medium for best removal of nickel is generally somewhat acidic, and this condition may be brought about, at least initially, by the presence of an acid-acting salt or some entrained acidic oxidizing agent on the catalyst. The aqueous medium can contain extraneous ingredients in trace amounts, so long as the medium is essentially water and the extraneous ingredients do not interfere with demetallization or adversely affect the properties of the catalyst. Ambient temperatures can be used in the wash but temperatures of about 150° F., to the boiling point of water are sometimes helpful. Pressures above atmospheric may be used but the results usually do not justfy the additional equipment. Where an aqueous oxidizing solution is used, the solution may perform part or all of the metal compound removal simultaneously with the oxidation. In order to avoid undue solution of alumina from a chlorinated catalyst, contact time in this stage is preferably held to about 3 to 5 minutes which is sufficient for nickel removal. Also, since a slightly acidic solution is desirable for nickel removal, this wash preferably takes place before the ammonium wash.

Alternative to the removal of poisoning metals by procedures involving contact of the sulfided or sulfated catalyst with aqueous media, nickel poison may be removed through conversion of the nickel sulfide to the volatile nickel carbonyl by treatment with carbon monoxide, as described in copending application Ser. No. 47,598. In such a procedure the catalyst is treated with hydrogen at an elevated temperature during which nickel contaminant is reduced to the elemental state, then treated, preferably under elevated pressure and at a lower temperature with carbon monoxide, during which nickel carbonyl is formed and flushed off the catalyst surface. Hydrogenation takes place at a temperature of about 800 to 1600° F., at a pressure from atomspheric or less up to about 1000 p.s.i.g. with a vapor containing 10 to 100% hydrogen. Preferred conditions are a pressure up to about 15 p.s.i.g. and a temperature of about 1100 to 1300° F. and a hydrogen content greater than about 80 mole percent. The hydrogenation is continued until surface accumulations of poisoning metals, particularly nickel, are substantially reduced to the elemental state. Carbonylation takes place at a temperature substantially lower than the hydrogenation, from about ambient temperature to 300° F. maximum and at a pressure up to about 2000 p.s.i.g. with a gas containing about 50 to 100 mole percent CO. Preferred conditions include greater than about 90 mole percent CO, a pressure of up to about 800 p.s.i.g. and a temperature of about 100 to 180° F. The CO treatment serves generally both to convert the elemental metals, especially nickel to volatile carbonyls and to remove the carbonyls.

After the ammonium wash, or after the final treatment which may be used in the catalyst demetallization procedure, the catalyst is conducted back to the cracking system. Where a small amount of the catalyst inventory is demetallized, the catalyst may be returned to the cracking system, preferably to the regenerator standpipe, as a slurry in its final aqueous treating medium. Where a large amount of catalyst inventory is treated, lest the water put out the fire or unduly lower the temperature in the regenerator, it may be desirable first to dry a wet catalyst filter cake or filter cake slurry at say about 250 to 450° F. and also, prior to reusing the catalyst in the cracking operation it can be calcined, say at temperatures usually in the range of about 700 to 1300° F. Prolonged calcination of the catalyst at above about 1100° F. may sometimes be disadvantageous. Calcination removes free water, if any is present, and perhaps some but not all of the combined water, and leaves the catalyst in an active state without undue sintering of its surface. Inert gases such as nitrogen frequently may be employed after contact with reactive vapors to remove any of these vapors entrained in the catalyst or to purge the catalyst of reaction products.

The demetallization procedure of this invention has been found to be highly successful when used in conjunction with fluidized catalytic cracking systems to control the amount of metal poisons on the catalyst. When such catalysts are processed, a fluidized solids technique is recommended for these vapor contact demetallization procedures as a way to shorten the time requirements. Any given step in the demetallization treatment is usually continued for a time sufficient to effect a substantial conversion or removal of poisoning metal and ultimately results in a substantial increase in metals removal compared with that which would have been removed if the particular step had not been performed. After the available catalytically active poisoning metal has been removed, in any removal procedure, further reaction time may have relatively little effect on the catalytic activity of the depoisoned catalyst, although further metals content may be removed by repeated or other treatments.

This invention will be better understood by reference to the drawings. FIGURE 1 has already been described. It is to be understood that the particular apparatus described is illustrative only and not limiting.

FIGURE 2 is a schematic representation of the process of this invention which employs a hydrogenolysis or a vis-breaking step to produce further quantities of gas oil from the extraction raffinate.

FIGURE 3 is a schematic representation of a fluid catalytic cracking system having associated with it components of a demetallization unit which may be used in the system of this invention.

The solvent treating process may be carried out in a conventional solvent extraction tower. Batch mixing and settling may be employed or continuous and countercurrent treating operations may be employed. For instance, as represented in FIGURE 2, it is preferred to carry out the extraction process of this invention by introducing an extraction solvent such as a propane-butane mixture to a lower portion of treating tower **8**, via line **10**, to flow upwardly counter-current to vacuum asphalt or other heavy residua containing extractable gas oils to be treated, which is introduced near the top of the extraction tower via line **12**. Packing elements, perforated plates, or other contacting aids can be employed in such a system. An extract phase constituting the treated gas oil components and most of the propane-butane mixture may be removed overhead from such a tower via line **14**. A raffinate phase, comprising deoiled asphalt containing metal contaminants and little solvent is removed from the bottom of the tower via line **16**.

The extract phase constituting the deasphalted gas oil and solvent is treated in separation zone **18**, permitting removal of the extracting solvent and passage of the deasphalted gas oil (DAGO) via line **20** to the catalytic reactor **22**. The raffinate phase may be withdrawn from the system by line **24** or may be sent by line **26** to raffinate separator **28** for removal of any solvent entrained in the raffinate. Solvent may be recovered from the extract and raffinate phases by conventional techniques as described above and recycled to the extraction zone by lines **30** and **32** from the extract and raffinate separators, respectively.

The raffinate is drawn from the separator by line **34** and passed either to a visbreaking operation by line **36** or to a hydrogenolysis operation by line **38**. Visbreaker **40**, generally comprises the cracking coil **42**, which may be enclosed within the heating jacket **44**. The thermally cracked products may be withdrawn from the visbreaker by line **46**.

In hydrogenolysis unit **48** the deoiled asphalt is subjected to the action of hydrogen from the line **50** in the presence of a hydrogenation catalyst as described above. The hydrogen may be supplied by recycle from the line **52** and/or from an external source by line **54**. The products of hydrogenolysis are drawn from the reactor by line **56**.

Line **58** brings the products of hydrogenolysis or visbreaking to the fractionator **60** where these products are separated into gas oil components which are drawn off by line **62** for passage to the cracker **22**. The combined gas oil fractions from the deasphalting unit **8** and the fractionator **60** may be diluted with gas oil from line **21**, which is substantially free of metal poisons, and derived from previously mentioned internal or external sources. Heavy products are drawn from fractionator **60** by line **64** and discarded from the system by line **66** or recycled by line **68** to the visbreaker or to the hydrogenator by line **70** or to the deasphalting unit by line **72**.

The catalytic cracking system comprises the reactor **22** and the regenerator **74**, and is provided with lines **76** and **78** for passage of catalyst to and from the regenerator, respectively. In this invention there is also provided a demetallization unit **80** with lines **82** and **84** for passage of the catalyst to and from the demetallization unit, respectively. Cracked products leave reactor **22** by line **86** for passage to the fractionator **88**, wherein these cracked products are separated as desired. Hydrogen-rich gases, if

any, leave the fractionator by line 52 for recycle to the hydrogenolysis unit when such is employed. The fractionator is provided with line 90 for the removal of gasoline, etc., products. The 400° F. plus boiling components may be removed by line 92 for recycle to the visbreaker or hydrogenolysis by line 94 or to the solvent extractor by line 72. As mentioned, the gas oil fraction may be separated from the 400° F. plus product and recycled to the cracking feed by means not shown.

The cracking and demetallization systems are shown in further detail in FIGURE 3. This figure shows apparatus suitable for performing the cracking, regeneration and demetallization using a fluidized solids technique. The operation is as follows:

The reactor and the catalyst regenerator are or may be arranged at approximately an even level. An overflow is provided in the regeneration zone at the desired catalyst level. The catalyst overflows into a withdrawal line 100 which preferably has the form of a U-shaped seal leg connecting the regeneration zone with the reaction zone. The feed stream introduced at 102 by line 20 is usually preheated to a temperature in the range from about 500° to 650° F. by heat exchange with cracked products. The heated feed stream is then introduced into the reactor by line 78. The seal leg is usually sufficiently below the point of feed oil injection to prevent oil vapors from backing into the regenerator in the case of normal surges. Since there is no restriction in the overflow line from the regenerator, satisfactory catalyst flow will occur as long as the catalyst level in the reactor is slightly below the catalyst level in the regenerator when the vessels are maintained at about the same pressure. Spent catalyst from the reactor flows through a second U-shaped seal leg 104 from the bottom of the reactor 22, to the regenerator 74. The rate of catalyst flow is controlled by injecting air at 106 into the catalyst transfer line 76 to the regenerator 74 which may be provided with the exit 108 for exhaust gases.

A small slip-stream of catalyst may be removed from the standpipe 100 for demetallization by line 82. The drawing in FIGURE 3 illustrates a demetallization system which includes apparatus for elevated temperature treatment with oxygen, sulfiding, chlorinating, washing and filtering the catalyst. The catalyst may be withdrawn from regenerator standpipe 100 by line 82 which brings it to oxygen treater 110, where the catalyst is held at elevated temperatures in contact with air or other oxygen-containing gas from the line 111. Pipe 112 conducts the catalyst to sulfider 114. In the sulfider the catalyst is contacted as a fluidized bed with sulfiding vapors entering by line 116. Catalyst exits by line 118 and waste sulfiding gas exits by line 120. Line 118 brings the catalyst to chlorinator 124 where it is contacted with chlorinating vapor entering from line 126. Exhaust chlorinating vapor and vaporized metal poisons leave by line 128 and the catalyst, reduced in vanadium content passes by line 130 to slurry tank 132 which is kept supplied with water, perhaps containing pH-adjusting components, from the line 134. Agitation is maintained in the slurry tank by suitable means not shown and the slurry is quickly withdrawn by line 136 to the filter 138. Although shown as a rotary drum filter, it may be of any desired type. The filter produces a catalyst cake which may be washed by water from the source 140 and scraped from the filter by doctor blade 142. Excess aqueous material is removed from the system by line 144. Catalyst goes by route 146 to wash tank 148. A slurry of catalyst in wash water may be brought by line 84 back to regenerator 74.

Alternatively the sulfided catalyst may be removed from the sulfider 114 via line 150 and conveyed to oxidizing tank 152 which is kept supplied with a liquid oxidation agent, hereinbefore described, through line 154. The sulfided catalyst is agitated with the oxidizing agent and is withdrawn by line 156 to the filter 138, where the catalyst is treated as previously described. Another alternative demetallization pocedure is to remove the poisoned catalyst from oxygen treater 110 by line 158 to a slurry tank 160 where the catalyst is washed with a basic aqueous solution containing ammonium ions which is introduced via line 162. The slurry is withdrawn by line 164 and conveyed to the filter 138.

The present invention will be further described with reference to the following examples which are not to be considered limiting.

Example I

A Mid-Continent asphalt fraction boiling above 400° F. and having the following characteristics:

Specific gravity 60/60° F.	0.9907
Penetration at 77° F.	179
Viscosity, FV/210° F.	517
Ring and ball softening point, ° F.	106
Benzene insolubles	0.96
Sulfur, wt. percent	0.91

is extracted countercurrently in a tower with a solvent composition comprising 26.7 volume percent butane and 73.3 volume percent propane at 450 p.s.i.g. The tower temperature is 108° F. at the bottom (raffinate) outlet and 140° F. at the top (extract) outlet. The solvent-to-oil ratio is 6.8/1 vol./vol. which is about twice as much solvent-to-oil as gives a minimum recovery. See FIGURE 1. The extraction yields approximately 45 volume percent, based on the amount of feed used, of a gas oil product having the characteristics reported in Table IV below. This gas oil, containing 1.92 p.p.m. nickel and 3.12 p.p.m. vanadium, reported as common oxides, is passed to a fluid catalytic cracking unit under the following conditions:

Fresh feed rate	30 lbs./hr.
Catalyst/oil ratio	8/1.
Reactor temperature	960° F.
Stripping steam	16 wt. percent on feed.
Carrier steam	10 wt. percent on feed.
Carbon on regen. cat.	0.3 wt. percent.
Catalyst composition synthetic silica-alumina (17% Al_2O_3).	

The equilibrium conversion and yields are given in Table IV below. Also reported, for comparison, are the characteristics of a convention gas oil and the yields obtained under similar cracking conditions as the deasphalted gas oil.

It was determined that a metals level of 300 p.p.m. NiO was the tolerance of the cracking unit for economic processing of the deasphalted gas oil. About 15% of the cracking catalyst inventory is each day sent as a side stream from the regenerator to demetallization. The catalyst is at the equilibrium metals level of about 300 p.p.m. nickel and 1740 p.p.m. V_2O_5 and contains about 0.4% carbon. In the demetallization process the catalyst is held in air for about an hour at about 1300° F. and then sent to a sulfiding zone where it is fluidized with H_2S gas at a temperature of about 1150° F. for about 1½ hours. The catalyst is cooled and purged with inert gas and chlorinated with an approximately equimolar mixture of Cl_2 and CCl_4 at about 600° F. After about one hour no trace of vanadium chloride can be found in the chlorination effluent and the catalyst is quickly washed with water. A pH of about 3 is imparted to this wash medium by chlorine contained in the catalyst and the wash serves to remove nickel chloride. The catalyst with 20% of its vanadium and 70% of its nickel removed, is filtered from the wash slurry, dried at about 350° F. and returned to the regenerator.

Example II

Feedstock C, described in Table I above, was sent to a solvent extraction tower and contacted countercurrently at a pressure of about 400 p.s.i.g. with 4 parts per part of feedstock of a solvent composition comprising about 20 volume percent butane and 80 volume percent pentane.

This is a smaller solvent-to-oil ratio than gives minimum gas oil recovery. See series VII of FIGUURE 1. A temperature of 230° F. is maintained at the extract outlet at the top of the tower and 190° F. at the bottom. The yield was about 82.4 volume percent of a gas oil having the characteristics reported in Table IV below.

The Mid-Continent deasphalted gas oil from the extraction tower is removed to a separator where the solvent is removed and recycled back to the solvent extraction tower. The deasphalted oil having the properties shown in Table IV is fed to a fluid catalytic cracking unit and is run under the same conditions in Example I, in conjunction with a demetallization unit.

The catalyst is continually sent to a regenerator, where it is contacted with air at 1050° F. to burn off the carbon. A side stream of the regenerated catalyst having a carbon content of about 0.4%, 300 p.p.m. nickel and 2000 p.p.m. vanadium is continuously removed from the regenerator at a rate of about 215% of inventory daily and sent to an oxygen treating unit where it is held for about an hour in contact with air at about 1300° F. and then sent to a sulfiding zone where it is fluidized with H_2S gas at a temperature of about 1150 for about 1½ hours. The catalyst is cooled and purged with inert gas and chlorinated with an equimolar mixture of Cl_2 and CCl_4 at about 600° F. After about 1 hour no trace of vanadium chloride can be found in the chlorination effluent and the catalyst is quickly washed with water. A pH of about 3 is imparted to this wash medium by chlorine entrained in the catalyst and the wash serves to remove nickel chloride.

The catalyst substantially reduced in nickel and vanadium content is filtered from the wash slurry, dried at about 350° F. and returned to the regenerator. The demetallization procedure removes about 70% nickel and about 20% vanadium.

TABLE IV

	Conventional M.C. Gas Oil	Example I	Example II
Solvent Extraction:			
Solvent, percent:			
Butane		26.7	20
Propane		73.3	
Pentane			80
Gas oil yield (based on feed)		45	82.4
Solvent/feed ratio		6.8	4.0
Product gas oil:			
Gravity, ° API	27.3	21.3	14.8
Pentane insolubles, Wt. percent		1.93	1.13
Aver. Mol. Wt.		1,032	1,019
Carbon residue (Conradson)	0.252	3.75	12.26
NiO, p.p.m.	0.34	1.92	24
V_2O_5, p.p.m.	1.86	3.12	46
Cracking Conversion:			
Conversion of gas oil	65.0	65.0	65
C_5-EP gasoline, Vol. Percent (on gas oil)	46.4	56.0	44.6
C_5-EP gasoline, Vol. Percent (on feed to solvent extraction)		25.2	36.5
Total C_4, Vol. Percent	16.8	11.6	10.0
C_3 minus, Wt. Percent	9.2	7.3	9.1
Coke, Wt. Percent	4.6	5.2	15.1
Hydrogen, s.c.f. (bbl.)	44.0	38.5	205
Light cycle oil Vol. Percent	24.2	25.9	20.7
Heavy cycle oil, Vol. Percent	19.4	11.1	14.3
Light cycle oil, Gravity, °API	19.3	20.4	22.6
Heavy cycle oil, Gravity, ° API	15.7	14.6	4.4

It will be observed from this data that the process of this invention which employs a solvent-to-oil ratio lower than that at which a minimum yield is obtained in extraction and catalyst demetallization gives cracking results essentially as good as methods which use more solvent to produce a less poisoned cracking feed. It will also be seen that this invention provides much greater amounts of cracking feed and therefore much greater amounts of gasoline, etc., from a given amount of residual.

Example III

Feedstock B, described in Table I above, was sent to a solvent extraction tower and contacted countercurrently at a pressure of 500 p.s.i.g. with 3.4 parts per part of feedstock of a solvent composition comprising about 22.4 volume percent butane and 77.6 volume percent propane.

This is a smaller solvent-to-oil ratio than gives a minimum gas oil recovery. See series V of FIGURE 1. A temperature of 145° F. is maintained at the extract outlet at the top of the tower and 105° F. at the bottom. The yield was about 50 volume percent of a gas oil having the characteristics reported in Table V below. The extracted oil containing 3.45 p.p.m. NiO and 7.55 p.p.m. V_2O_5 was passed to the cracking unit operated at the following conditions:

TABLE IV

Fresh feed rate	30 lbs./hr.
Catalyst/oil ratio	8/1.
Reaction temperature	910° F.
Stripping steam	16 wt. percent on feed.
Carrier steam	10 wt. percent on feed.
Carbon on regen. cat.	0.03 wt. percent.
Catalyst composition	Synthetic silica-alumina (15% Al_2O_3).
Catalyst inventory	200 lbs.

The equilibrium conversion and yields are given in Table V.

About 39% of the cracking catalyst inventory containing 240 p.p.m. NiO and 1800 p.p.m. V_2O_5 is each day sent as a side stream from the regenerator to demetallization. In the demetallization process the catalyst is held in air for about an hour at about 1300° F. and then sent to a sulfiding zone where it is fluidized with H_2S gas at a temperature of about 1175° F. for about 1 hour. Dilute nitric acid is brought in contact with the sulfided catalyst and the slurry is aerated for about 10 minutes at a temperature of 200° F. to convert nickel poisons to dispersible form and remove them. The catalyst is then washed with an ammonium hydroxide solution having a pH of about 8 to 11, removing the available vanadium. The catalyst, substantially reduced in nickel and vanadium content is filtered from the wash slurry, dried at about 350° F. and returned to the regenerator. The treated catalyst analyzes a metals content of 96 p.p.m. nickel and 1314 p.p.m. vanadium.

The deoiled asphalt is passed to a visbreaker operated at the following conditions:

Tower pressures ——p.s.i.g	30
Heater pressures ——p.s.i.g	53
Heater temperatures:	
1st section ——° F	730
2nd section ——° F	908
3rd section ——° F	908
4th section ——° F	910
5th section ——° F	910

The yield from the visbreaker is shown in Table V below. This combined process provides a 31 volume percent yield of C_5-EP gasoline and the visbreaker produces 9.8 volume percent more gas oil which may be combined with the gas oil from the extraction step and catalytically cracked to provide increased amounts of lower boiling materials.

Example III

TABLE V

Solvent extraction:	
Solvent—	
Butane, percent	22.4
Propane, percent	77.6
Solvent/feed ratio	3.4
Gas oil yield (based on feed)	50
Product gas oil:	
Gravity, ° API	20.1
Petane insolubles, wt. percent	0.15
Aver. mol. wt.	999
carbon residue (Conradson) wt. percent	4.043
NiO, p.p.m.	3 45
V_2O_5 p.p.m.	7.55

Product Asphalt:	
Specific gravity 60° F./60° F.	1.0538
Penetration, 77° F.	4
Carbon residue (Conradson) wt. percent	31.1
Viscosity FV/350° F.	196.6
Pentane insolubles, wt. percent	32.0
Sulfur, wt. percent	1.23
Cracking conversion of DAGO:	
Conversion of gas oil	65
C_5-EP gasoline, vol. percent (on gas oil)	54.6
C_5-EP gasoline, vol. percent (on feed to solvent extraction)	27.3
Total C_4, vol. percent	11.4
C_3 minus, vol. percent	5.9
Coke, wt. percent	7.8
Light cycle oil, vol. percent	20.2
Heavy cycle oil, vol. percent	14.8
Light cycle oil gravity, ° API	25.1
Heavy cycle oil gravity, ° API	10.2
Visbreaker conversion of deoiled asphalt:	
Conversion of deoiled asphalt, vol. percent	27.3
Gas oil, vol. percent (on feed to visbreaker)	19.6
C_5-EP gasoline, vol. percent (on feed to visbreaker)	7.3
Total C_4, vol. percent	1.1
C_3 minus, wt. percent	1.4

A good understanding of the advantages of the instant invention can be gained from a consideration of the following demonstration commercial applications of the process, which show that control of the amount of metal contaminants entering the cracking system is necessary for the economic exploitation of contaminated feed.

These demonstration cases employ, as a feed to the deasphalter, asphaltic residuum A of Table I. The solvent deasphalting operation used solvent K of Table II, a liquefied mixture of 85% propane and 15% butane, which mixture is also represented in FIGURE 1 by the curve identified as series II, feed A, solvent K.

These demonstration operations are based upon the availability of a conventional cracking feedstock for dilution of the deasphalted gas oil. This conventional feedstock contains about 0.4 p.p.m. nickel and 0.8 p.p.m. vanadium measured as the common oxides. The catalyst employed is a synthetic gel, silica-alumina catalyst which is to be kept at a metal level of 300 p.p.m. NiO or less. The demetallization unit removes about 50% of the nickel on the catalyst and about 15% of the vanadium. Thus, when operating at this efficiency with a catalyst containing the maximum allowable amount of nickel, 150×10^{-6} pounds of nickel as NiO and 90×10^{-6} pounds of vanadium as V_2O_5 can be removed from each pound of catalyst treated.

In demonstration case X, a feedstock is prepared having less than the 1 p.p.m. nickel and less than the 2 p.p.m. vanadium component required. This feedstock is prepared by blending three parts of the conventional feedstock with the DAGO product obtained from one part of residual by the procedure of Run 2, Table III which run produced the least poisoned DAGO. This DAGO was 53.3 volume percent of the residual and had a Conradson carbon of 3.8 and 2.2 p.p.m. NiO and 1.9 p.p.m. V_2O_5. The fluid feed mixture has the following characteristics:

	Parts of Total Feed	P.p.m. NiO	P.p.m. V_2O_5	NiO Product	V_2O_5 Product
Conventional feedstock	3.0	0.4	0.8	1.2	2.4
Deasphalted gas oil	0.533	2.2	1.9	1.17	1.02
	3.533			2.37	3.42

P.p.m. NiO per part of feed—$(2.37\div3.533)=0.6$
P.p.m. V_2O_5 per part of feed—$(3.42\div3.533)=0.96$
Lbs. NiO per barrel (315 lbs.) of feed:
$(0.6\times10^{-6}\times315)=189\times10^{-6}$
Lbs. V_2O_5 per barrel (315 lbs.) of feed:
$(0.96\times10^{-6}\times315)=300\times10^{-6}$

Since the demetallization unit can remove 150×10^{-6} p.p.m. of NiO for each pound of catalyst treated, only 1.38 lb. of catalyst (189/150) needs to be treated per barrel of feed. When it is considered that the same amount of nickel can be removed from the system by discarding and replacing with virgin catalyst half the amount to be demetallized, that is, only 0.69 pound of catalyst per barrel of feedstock, it is clear that catalyst discard and replacement would be cheaper than the capital and operating expenses of a demetallization unit. Also, the deasphalter operation would be prohibitively expensive in most refinery operations because of the high solvent to feed ratio (7.1 to 1) required. The recovery of the solvent is often the major operating expense involved in deasphalting.

In demonstration case Y, a cracking feedstock having more metal than allowed is employed. This feedstock is the undiluted DAGO produced in Run 4, Table III, i.e. 75.1 volume percent of the residual feed with a Conradson carbon of 13.4 and 32.4 p.p.m. NiO and 73.7 p.p.m. V_2O_5.
Lbs. NiO/bbl. of feed $(32.4\times10^{-6}\times315)=10300\times10^{-6}$
Lbs. V_2O_5/bbl. of feed $(73.7\times10^{-6}\times315)=23000\times10^{-6}$
In this case, the demetalization system would need to treat 10300/150 or 69 pounds of catalyst per barrel of feed. While such demetallization would be a great saving over 34.5 pounds of catalyst per barrel of feed which would otherwise need be removed and replaced with virgin catalyst, it would require a catalyst demetallization apparatus of enormous size. Each of the demetalization vessels would need to be near the size of the average commercial regenerator.

Also, in case Y, a number of other disadvantages would appear in the conversion operation, for example, the amount of coke precursors would be excessive as witnessed by the high Conradson carbon of the DAGO and vanadium would build up rapidly on the catalyst leading to greater hydrogen production in cracking and lowering the yield of stable products. Also, the much higher vanadium level on the catalyst would catalyze CO conversion to CO_2 in the regenerator, thus greatly increasing the oxygen consumption and consequent air requirement in regeneration.

In demonstration case Z, the cracking feedstock has a metal content within the limits set forth in the appended claims. It is prepared by blending two parts of conventional feed with the DAGO product of one part of residual. The deasphalted gas oil product is made as in Run 1, Table III, i.e. 52.0 volume percent yield of DAGO with a Conradson carbon of 5.7 and 9 p.p.m. NiO and 9 p.p.m. V_2O_5. The total feed has the following characteristics:

	Parts of Total Feed	P.p.m. NiO	P.p.m. V_2O_5	NiO Product	V_2O_5 Product
Conventional feed	2	0.4	0.8	0.8	1.6
Deasphalted gas oil	0.52	9	9	4.67	4.67
	2.52			5.47	6.27

P.p.m. NiO per part of feed $(5.47\div2.52)=2.16$
P.p.m. V_2O_5 per part of feed $(6.27\div2.52)=2.55$
Lbs. NiO per barrel of feed $(2.16\times10^{-6}\times315)=680\times10^{-6}$
Lbs. V_2O_5 per barrel of feed $(2.55\times10^{-6}\times315)=810\times10^{-6}$

In this case Z the demetallization system would need to treat 680/150 or 4.5 lb. of catalyst per barrel of feed processed. This represents a great saving over 2.25 lb. of catalyst per barrel of feed which would need be discarded were the demetallization system not employed, while requiring a demetallization apparatus of moderate size and operating expense, i.e. about $\frac{1}{15}$ the size needed in case Y. Also, the deasphalted gas oil stock of case Z

is only marginally higher in Conradson carbon than that of case X while being of approximately the same yield. Deasphalting is accomplished at a solvent-to-oil ratio of 3/1 rather 7.1/1 as in case X. The solvent-to-oil ratio of case Z is sufficiently lower to show a distinct economic advantage for the deoiler operation over a case X.

Also, it can be seen from FIGURE 1 that case X represents a deasphalter operation in which the solvent-to-oil ratio (7.1) is greater than that at which a minimum yield is obtained and that the case Z represents a deasphalter operation in which the solvent-to-oil ratio (3.0) is less than that at which a minimum yield is obtained. These regions of operations are ones in which the phase relation between the extract and raffinate phases are different, case X being representative of the region of operations in the industry today, while case Z is representative of the region in which the industry does not operate.

What is claimed:

1. In a process for treating a residual hydrocarbon oil boiling above the gasoline range containing at least about 15 parts per million of nickel and at least about 25 parts per million of vanadium, wherein the said hydrocarbon oil is contacted in a deasphalting zone with a low boiling, liquid hydrocarbon solvent to form a deasphalted gas oil phase and an asphalt phase, a hydrocarbon feedstock comprising at least about 10% of the resulting deasphalted gas oil phase is subjected to fluidized catalytic cracking with a synthetic gel, silica-based catalyst, the cracked products, including gasoline, are recovered from said cracking zone and carbon is burned from the catalyst to regenerate the catalyst, the improvements which comprise confining the amount of liquid hydrocarbon solvent to an amount lower than the solvent-to-oil ratio at which a minimum yield of gas oil is obtained, so that the deasphalted gas oil contains at least about 1.5 p.p.m. nickel and at least about 2 p.p.m. vanadium, providing a cracking feedstock containing about 1 to 30 p.p.m. nickel and about 2 to 60 p.p.m. vanadium and bleeding from the cracking system a portion of catalyst containing at least about 200 p.p.m. nickel and at least about 500 p.p.m. vanadium, demetallizing bled catalyst to remove at least about 50% of the nickel and at least about 15% of the vanadium, and returning demetallized catalyst to the cracking-regeneration system, said metal levels being measured as NiO and V_2O_5, respectively.

2. The method of claim **1** in which the residual oil is unvisbroken.

3. The process of claim **1** in which demetallizing includes contact of the catalyst with a vapor reactive with a metal contaminant.

4. The process of claim **1** wherein the low-boiling hydrocarbon is selected from a group consisting of propane-butane and butane-pentane mixtures.

5. The process of claim **4** wherein the low-boiling liquid hydrocarbon mixture comprises about 10–50% butane.

6. The process of claim **1** wherein the asphalt phase is conducted to a hydrogenolysis unit where the asphalt phase is subjected to hydrogenation at a temperature of 750 to 900° F. to produce a gas oil containing about 50 to 90% less of nickel and vanadium than in said asphalt phase and the gas oil is combined with the deasphalted gas oil feed to the catalytic cracking zone.

7. The process of claim **1** wherein the asphalt phase is conducted to a visbreaking unit where the asphalt phase is thermally cracked at a temperature of about 800 to 950° F. to produce a gas oil, and the gas oil is combined with the deasphalted gas oil feed to the catalytic cracking zone.

8. The process of claim **1** wherein the catalyst is a fluidized synthetic gel silica-alumina catalyst.

9. The process of claim **1** in which the catalyst is silica-alumina and regenerated bled catalyst is demetallized by contacting regenerated catalyst with molecular oxygen-containing gas at a temperature of about 1000 to 1800° F. to enhance vanadium removal, sulfiding the metal-poisoned catalyst by contact with a vaporous sulfiding agent at a temperature of about 500 to 1500° F. to enhance nickel removal, chlorinating the sulfided catalyst by contact with an essentially anhydrous chlorinating agent at a temperature of about 300 to 1000° F., and contacting the chlorinated catalyst with a liquid, essentially aqueous medium to remove poisoning metal from the catalyst.

10. The process of claim **9** in which the sulfiding is performed by contact with H_2S.

11. The process of claim **10** in which the chlorinating is performed with an equimolar mixture of Cl_2 and CCl_4.

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