

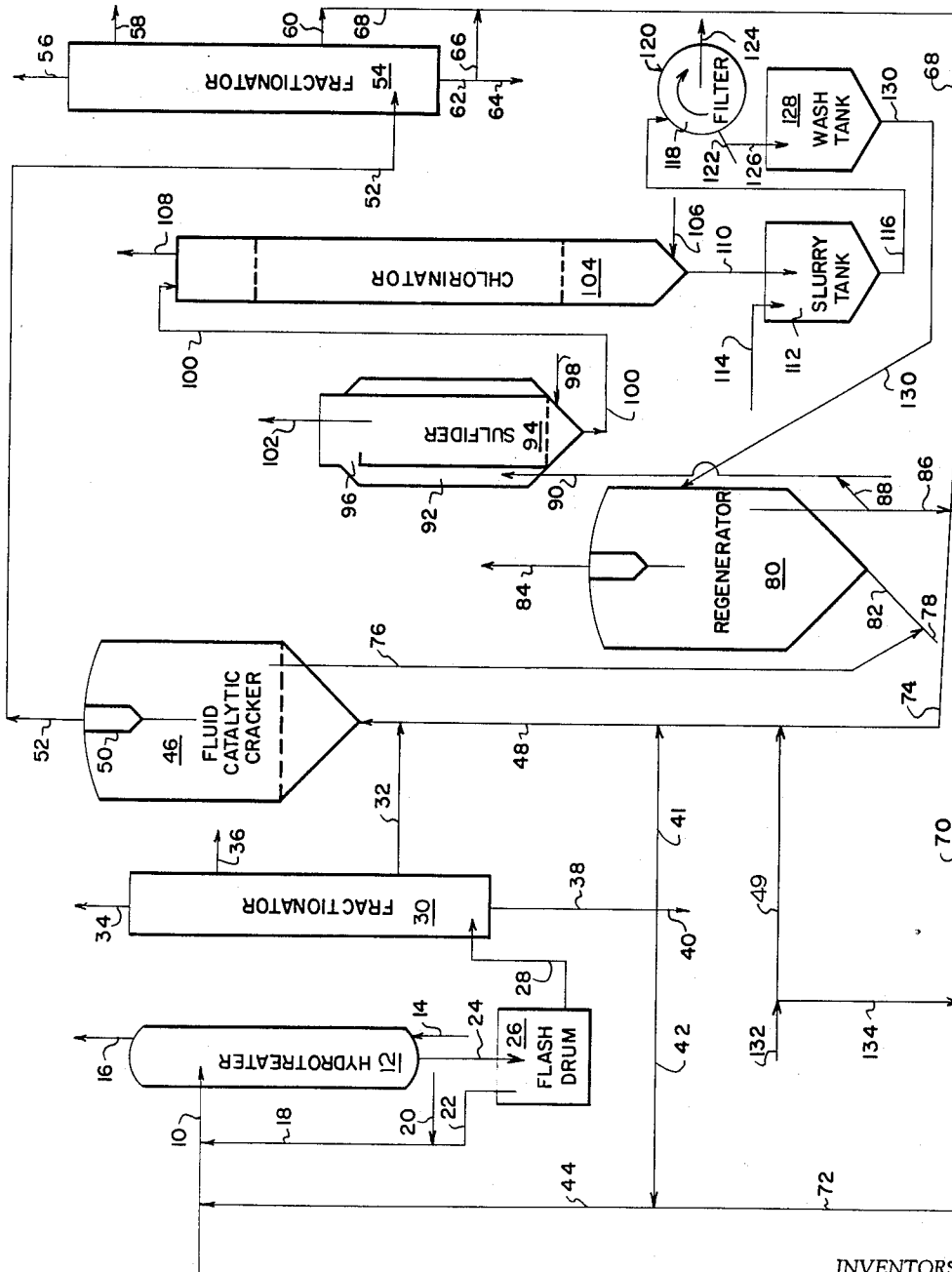
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CATALYTIC CRACKING OF MINERAL HYDROCARBON OIL

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3,168,461 CATALYTIC CRACKING OF MINERAL HYDROCARBON OIL

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This invention concerns the catalytic cracking of heavier mineral hydrocarbon oils to obtain lighter components including gasoline of relatively high octane number. More particularly, the invention relates to a process in which the results from hydrogenation and catalytic cracking of mineral hydrocarbon oils are improved.

The catalytic cracking of various heavier mineral hydrocarbons, for instance petroleum or other mineral oil distillates such as straight run and cracked gas oils; shale oils; petroleum residues; etc., has been proposed for many years and the catalytic cracking of gas oils is practiced commercially to a considerable extent. 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 includes any fraction distilled from petroleum or other mineral oil which has an initial boiling point of at least about 400° F., say, up to about 850° F., and an end boiling point of at least about 600° F., and boiling substantially continuously between the initial boiling point and the end boiling point. Usually the boiling range extends over at least about 100° F. The portion which is not distilled before the end point is reached 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 substantially continuously 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 about 400–1200° F. or it could boil over a narrower range, e.g., about 500–900° F.

The gas oils can be further roughly classified by boiling ranges. Thus, gas oil boiling between about 400–500° 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 any petroleum fraction higher boiling than a selected distillate fraction. Any fraction, regardless of its initial boiling point, which includes all the heavy bottoms, such as tars, asphalts, etc., may be termed a residual fraction. Accordingly, a residual stock can be the portion of the crude remaining undistilled at about 1100–1200° F., or it can be made up of a gas oil fraction plus the portion undistilled at about 1100–1200° F. For instance, a "whole topped crude," is the entire portion of the crude remaining after

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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 1100–1200° F.

The behavior of a hydrocarbon feedstock in the cracking reactions depends upon various factors including its boiling point, carbon-forming tendencies, content of catalyst contaminating metals, etc., and these characteristics may affect the operation to an extent which makes a given feedstock uneconomical to employ. By and large, residual stocks have not been catalytically cracked on a commercial scale as their carbon-forming tendencies and catalyst poisoning metals content are generally too great. Moreover, even some distillate materials need improvement in their hydrogen-to-carbon ratio or contain excessive amounts of metals which mitigates their usefulness in cracking. Frequently the refiner may take special cuts of distillate stocks or pretreat them prior to cracking in order that the catalytic cracking operation becomes more desirable overall even though by reducing the amount of cracking feed per barrel of crude oil the yield of gasoline is thereby reduced. Although the cracking catalyst employed in treating the hydrogenation product can be discarded more often to prevent a high accumulation of poisoning metals in the cracking system, this type of operation represents a substantial cost factor. Improvements in the feedstock characteristics become even more important as the cost of the catalyst rises and thus the effects of low feedstock quality are particularly burdensome in systems employing cracking catalysts containing relatively expensive synthetic components.

It has been proposed heretofore to hydrotreat the various heavy metal-containing hydrocarbon oils prior to charging them, or a fraction thereof, to a catalytic cracking operation. By so doing the hydrocarbon may be given an improved hydrogen-to-carbon ratio and the amount of contaminants, such as coke-formers, sulfur, and nitrogen may be reduced. The content of metals which poison cracking catalysts is also reduced; these metals deposit on the hydrotreating catalyst. Removal of any substantial amount of these contaminants from the cracking feed tends to enhance efficiency of the catalytic cracking operation. The degree of feedstock improvement from hydrogenation is dependent, however, upon several factors which include the severity of reaction, hydrogen consumption and the activity decline of the hydrogenation catalyst during use. A fresh hydrogenation catalyst, for example, may remove the bulk of the metal contaminants even in low severity operations, but as the catalyst activity decreases metals removal will decline at a given severity. Increased severities can then be employed to maintain the desired extent of metals removal as the operation progresses. Increased severity, however, may involve a greater consumption of hydrogen, a larger capital investment for high-pressure equipment, and a reduction in the yield of cracking feedstock. Alternatively, the effect of metal contaminants in reducing the activity of the hydrogenation catalyst can be overcome by discarding this catalyst more often. Either of these alternatives increases the cost of hydrogenation substantially.

The present invention comprises hydrotreating a petroleum hydrocarbon feedstock boiling above the gasoline range to achieve substantial demetallization of the feed, catalytically cracking the hydrotreated oil or a portion

thereof, including material boiling above the gasoline range, perhaps in combination with cracking feedstock components from external sources, and demetallizing the cracking catalyst. In this way the effect of poisoning metals in a cracker feed can be essentially obliterated. A balance between partial demetallization of cracking feed components in the hydrotreating and demetallizing the cracking catalyst by procedures to be described, achieves greater economy than would be obtained by employing only one of the demetallizing techniques: hydrotreating or poison removal from the cracking catalyst, in the attempt to obviate poisoning effects.

In this invention an operation involving hydrotreating and catalytic cracking of heavier mineral hydrocarbon oil feedstocks to produce gasoline can be combined with a procedure for reducing poisoning metals on the cracking catalyst to present a much more attractive alternative to the operations described above for overcoming an overall metals problem. Under these conditions all three of the hydrotreating, catalytic cracking and cracking catalyst demetallization can be operated to make a relatively low consumption of hydrogen during hydrogenation more attractive, with the hydrogen being better utilized through minimization of dehydrogenation in the catalytic cracking operation. In this method the metal-containing hydrocarbon feedstocks is hydrotreated under conditions giving a desired hydrogenation effect with partial, but not complete, removal of poisoning metals. The hydrotreated oil or a selected portion thereof containing a significant amount of metal contaminant is then catalytically cracked by itself or after blending with conventional cracking feedstocks, to produce in good yield a gasoline fraction of relatively high octane rating. As the cracking operation proceeds the catalyst is treated to remove accumulated metal poisons and is then reused in the cracking operation. Besides preserving the effects of hydrotreating, by minimizing the dehydrogenation effects of a poisoned catalyst, catalyst demetallization provides a cracking operation in which there is relatively less carbon laydown on the catalyst. This further increases gasoline yield in a system having a given carbon-burning capacity.

In the hydrotreating operation a petroleum feedstock is contacted with a catalyst in the presence of free hydrogen under superatmospheric pressure. The hydrogenation catalysts generally known in the art can be employed. Calcined solid hydrogenation catalysts are preferred and they are usually disposed as a fixed bed of macrosized particles, say of about $\frac{1}{8}$ " to $\frac{1}{4}$ " in diameter and about $\frac{1}{8}$ " to 1" or more in length. A moving bed of macrosized catalyst or a fluidized bed of finely divided particles can also be used. The catalyst contains catalytically active amounts of a hydrogenation promoting metal, for instance a heavy metal component such as those of metals having atomic numbers of about 23 to 28, the Group VIII catalysts of the platinum and iron groups, molybdenum, tungsten and combinations thereof. Frequently the metals are disposed as inorganic components, for instance oxides, sulfides or other compounds, supported on a solid carrier exemplified by alumina, silica, etc. Advantageously, the catalyst contains a combination of metals of the iron group with vanadium or a metal of Group VIa of the periodic chart having atomic numbers from 42 to 74, i.e., molybdenum and tungsten. A commercial catalyst contains cobalt and molybdenum, e.g., cobalt molybdate, supported on alumina. The amount of catalytically active metal in the supported catalysts is usually about 1 to 30 weight percent of the catalyst and preferably about 3 to 20 weight percent, with there being at least about 1%, preferably at least about 2%, of each catalytically active metal when combinations are used.

In the hydrotreating operation metal poisons contained in the feedstock deposit on the hydrogenation catalyst but usually this deprives the feedstock of no more than about

90% of its metal content. Also, there is generally deposition of coke on the catalyst which can be removed by continuous or intermittent regeneration, that is, combustion of the coke by contact with oxygen. Regeneration does not remove poisoning metals deposited on the catalyst; however the common poisoning metals nickel and vanadium are of the same type as the original metal components of the hydrotreating catalyst. Therefore, small amounts of these metals do not usually poison, i.e., distort, the activity of these catalysts. As pointed out above, a sufficient accumulation of these metals may reduce the activity of these catalysts, so that very highly poisoned feedstocks quickly diminish the usefulness of the hydrotreating operation when conditions are maintained which deposit a large proportion of the poisoning metal on the catalyst.

In hydrotreating, the hydrogen has a number of effects on the feedstock. Its primary use in the process of this invention is to dissociate the heavy poisoning metals from their compounds in the feedstock. Hydrotreating may frequently serve to saturate components of the feed which are susceptible to such. Thus hydrotreating may increase the hydrogen-to-carbon ratio of the hydrotreater effluent and cracker feed, reducing the coke-forming tendencies of the feedstock. Also, hydrotreating generally causes a certain amount of the feed to be converted (cracked) to lower boiling materials. Extensive cracking in the hydrotreating operation may be desirable when a relatively heavy feedstock, e.g., a residual hydrocarbon oil is employed. The extent of cracking which takes place during hydrotreating is determined to a great extent by the temperature employed, higher temperatures in general giving a greater degree of cracking. Effective hydrotreating for demetallization and saturation may be achieved at a relatively low temperature when high pressures are used. If, however, the cost of the process are to be restricted and equipment suitable for withstanding less pressure used, a temperature sufficiently high to achieve the main objects of hydrotreating at lower pressure may be dictated. In such an eventuality, gas or gasoline produced by hydrocracking and unsuitable for use as feed to the catalytic cracking may be used as reformer feedstock.

With these factors in mind, the conditions of the hydrotreating operation may be chosen in view of the type of operation contemplated. Conditions are selected to give the desired hydrogen consumption and poisoning metals reduction. In general, however, an elevated temperature such as about 600 to 900° F. will be employed and the pressure will be superatmospheric usually falling in the range of about 300 to 3000 p.s.i.g. Free or molecular hydrogen is provided in the operation and generally in an amount of about 50 to 20,000 standard cubic feet per barrel of hydrocarbon oil feedstock, while the space velocity will lie in the area of about 0.1 to 10 or more WHSV (weight of hydrocarbon feedstock per hour per weight of catalyst).

In the hydrotreating operation there is always at least a minor amount of hydrogen which is consumed by chemical combination with a component of the hydrocarbon feed, and the extent of this consumption may depend upon the type of operation effected; that is, mere demetallization, saturation, or cracking. For instance, if the feedstock is quite undesirable as a charge to the catalytic cracking, preliminary hydrocracking can be obtained and the hydrogen consumption will be high, as in the case of treating most residual hydrocarbon oils. In this situation greater than about 10% of the hydrocarbon charge is usually converted to lower boiling normally liquid materials and quite frequently at least about 25% is converted. Conversion to lower boiling materials rarely exceeds 80% of a charge. Moreover, it may be most desirable to charge to the catalytic cracking operation only the distillate portion of the hydrotreater effluent, for instance, a gas oil fraction of the hydrocracked product, but

it is sometimes feasible to catalytically crack the entire hydrotreater effluent or the residual fraction thereof.

Where hydrocracking is minimized, such as in the treatment of a contaminated gas-oil fraction, the conversion of feed to lower boiling liquids is often less than about 10% and the hydrogen consumed reduces metals contamination and carbon-to-carbon bond unsaturation. The hydrocarbon oils treated in this relatively mild type of operation are usually distillate stocks, and essentially the entire normally liquid hydrotreated product can be charged to a catalytic cracking operation.

Hydrogen is supplied to the hydrotreating operation in amounts of from about 50 to 20,000 standard cubic feet per barrel of feed. Hydrogen consumption is usually at least about 70-300 standard cubic feet of hydrogen per barrel of hydrocarbon oil feed. Where hydrocracking is desired, such as in the treatment of residuals, the hydrogen consumption is often in the range of about 1000 to 2000 or more standard cubic feet per barrel, while in the milder hydrotreating of distillate stocks the hydrogen consumption will usually not be above about 100 to 300 standard cubic feet per barrel. The conditions of hydrotreating are generally a temperature of about 600-900° F., a superatmospheric pressure of about 300-3000 lbs. and a WHSV of about 0.1 to 10. When employing distillate feedstocks the reaction conditions are preferably about 600 to 800° F., about 500 to 1500 p.s.i.g., about 0.5 to 5 WHSV and about 50 to 5,000 standard cubic feet of hydrogen per barrel of feed. Residual oils will most often be treated at about 75 to 900° F., at a pressure over about 1000 p.s.i.g., preferably about 1500 to 2500 p.s.i.g., and about 100 to 10,000 standard cubic feet of hydrogen per barrel. The conditions of hydrotreating are adjusted to give the desired amount of metals removal from the feed, generally about 10 to 90% of the metal content of the feed. Preferably, the hydrotreating removes about 50-90% of the poisoning metals from a lightly contaminated feed or about 65-90% of the poisoning metals from a heavily contaminated feed. In spite of the amount of hydrogen consumed the metal contaminants of the feedstock, e.g., nickel, and/or vanadium, although decreased, are not reduced to a point insignificant to subsequent catalytic cracking.

The amount of metal to be removed from the feed is in turn, 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 mineral hydrocarbon oils charged to the hydrotreating operation are those materials which boil primarily above the gasoline range. These include the various distillate and residual stocks as noted above. Advantageous feedstocks are the petroleum gas oils which may be straight run or previously cracked stocks or their mixtures. Preferably, the charge to the hydrotreating operation contains a predominant amount of heavy mineral hydrocarbon oil boiling primarily in the range of about 650 to 1100° F. The hydrocarbon oils to which this invention is of primary applicability 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 feedstocks containing as little as about 0.4 p.p.m. nickel, and/or about 0.4 p.p.m. vanadium. The feedstock will usually include at least about 0.5 part per million of one or both of vanadium, and nickel. In distillate stocks vanadium is often present in amounts of at least about 1 to 2 p.p.m. and in addition nickel is frequently found along with the vanadium and in amount of at least about 0.2 to 1 p.p.m. The maximum amounts of these metals in distillate hydrocarbons will depend upon source, boiling range, etc., but usually the amounts will not exceed

about 3 p.p.m. nickel, and about 10 p.p.m. vanadium. Residual stocks are exemplified by reduced crude, atmospheric or vacuum distillation bottoms, etc., and will in general contain greater amounts of the poisoning metals than the distillate oils, for instance the residuals may contain as much as about 25 or 50 p.p.m. nickel, and about 50 or 100 p.p.m. vanadium. The maximum amount of metals in the residuals susceptible to the process of this invention can vary widely, particularly as upon hydrotreating only a distillate portion of the hydrotreated product may be charged to the catalytic cracking operation. Most often the maximum amount of these poisoning metals in the residual stock will not exceed about 50 p.p.m. nickel, and about 100 p.p.m. vanadium to be economically processed. Although referred to as "metals" the contaminants may be in the form of free metals or metal compounds and it is to be understood that the term "metal" used herein refers to either form.

As explained above, hydrotreating gives a partial reduction in metals content of the hydrotreated product. In this invention 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 or the portion used in cracking contains perhaps about 50-90 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, and vanadium will be about 60-90 weight percent.

The metal-containing hydrocarbon feedstock for the catalytic cracking operation can be all or a part of the hydrotreated product such as the entire gas oil fraction and the undistilled portion of the crude petroleum boiling above 1100-1200° F. or a selected fraction therefrom such as a fraction boiling within the gas oil range. Preferably the portion of hydrotreater effluent sent to cracking is a distillate fraction boiling in the gas oil range, for instance boiling primarily in the range of about 400 to 1100-1200° F., advantageously in the range of about 600 to 1100° F. Components of the hydrotreater effluent higher boiling than the fraction sent to catalytic cracking are conveniently recycled to the hydrotreating zone. The cracking feedstock boils above the gasoline range, and preferably boils primarily in the range of about 600-1100° F. The cracker feed comprises at least about 10% of hydrotreater effluent, preferably about 20-70%. 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 hydrotreating conditions and the proportion of hydrotreater effluent included in the cracker feed will be adjusted to provide a feed containing more than about 0.1 or 0.2 p.p.m. nickel and/or 0.3 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 less than about 10 p.p.m. nickel and/or 20 p.p.m. vanadium.

Catalytic cracking is ordinarily effected to produce gasoline as the most valuable product 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 5-15 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 the latter.

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 macrosized, 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 (fluidized) 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 operation 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 hydrotreating or catalytic cracking zones by blending them with virgin feed and/or hydrotreater effluent. 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 1/2%. 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 temperatures conducive to combustion. The regeneration does not remove from the catalyst the metals deposited from the cracking feed, which metals accumulate on the catalyst during the cracking operation. 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.

In the practice of this invention, catalyst demetallization is accomplished by the intermittent or continuous withdrawal of contaminated catalyst from the cracking system, for example, from the regenerator standpipe. 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. 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. Where the catalyst contains a greater amount of poisoning metal, a particular treatment will remove a greater amount of metal; it is advisable, therefore, to operate the cracking and demetallization procedures with a catalyst having a metals content near the limit of tolerance of the cracker for poisoning metals. This tolerance for poisoning metal oxide is seldom greater than about 5,000–10,000 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 metals level is allowed to exceed about 200 p.p.m. nickel and/or 500 p.p.m. vanadium so that total metals removal will be greater per pass through the demetallizer.

A suitable amount, generally a very small portion of the catalyst, is removed from the cracking system preferably after the oxidation regeneration which serves to remove carbonaceous deposits. With a continuously circulating catalyst stream, such as in the ordinary "fluid" system this may conveniently be done by the intermittent or continuous removal of a slip-stream of catalyst from the regenerator standpipe. The severity of regeneration is generally such that the catalyst sent to demetallization contains not more than about 0.5% carbon.

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 quantum of catalyst removed from the cracking system for demetallization is at the "equilibrium" metals level and is returned to the system at a lower metals level—about 10 to 90% lower, as mentioned above. Preferably a demetallization system is used which removes about 60 to 90% nickel and 20–40% 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.

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. The actual time or extent of treating depends on various factors, as mentioned, 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. The tolerance of the cracker for poison determines to a large extent the amount of metals removed in the catalyst demetallization procedure. 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.

The demetallization of the catalyst will generally include one or more processing steps wherein the catalyst is contacted, usually at an elevated temperature with a vapor reactive with the metal poison on the catalyst. Copending patent applications Serial Nos. 763,834, filed September 29, 1958, now abandoned; 842,618, filed September

28, 1959, now abandoned; 849,199, filed October 28, 1959; and 39,810, filed June 30, 1960, 47,598, filed August 4, 1960; 53,380, filed September 1, 1960, now U.S. Patent 3,122,497; 53,623, filed September 2, 1960; 54,368, filed September 7, 1960, now U.S. Patent 3,122,512; 54,405, filed September 7, 1960, now U.S. Patent 3,122,510; 54,532, filed September 7, 1960, now abandoned; 55,129, filed September 12, 1960; 55,160, filed September 12, 1960; 55,184, filed September 12, 1960, now abandoned and S. N. 55,703, filed September 13, 1960, all of which are hereby incorporated by reference. These applications 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.

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 Serial No. 19,313, filed April 1, 1960, now abandoned, 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 convert a substantial amount of vanadium to a higher 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% O₂. 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 patent applications

Serial No. 767,794, filed October 17, 1958, and Serial No. 39,810, filed June 30, 1960. Alternatively vanadium may be removed by a chlorination procedure as described in copending application Serial No. 849,199, filed October 28, 1959.

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 NH₄⁺ ions or organic-substituted NH₄⁺ ions such as methyl ammonium and quaternary hydrocarbon radical ammoniums. The amount of ammonium ion in the solution is sufficient 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 contaminants from the catalyst as volatile chlorides. This treatment is described in copending application Serial No. 849,199, filed October 28, 1959, incorporated herein by reference. 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 sometimes 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 1-40 percent 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 1-5 or 10 percent or more, preferably about 2-3 percent, 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 mixture may contain about 0.1 to 50 parts chlorine per part of promoter, preferably about 1-10 parts per part of promoter. A chlorinating gas comprising about 1-30 weight percent chlorine, based on the catalyst, together with one percent or more S₂Cl₂ gives good results. Preferably, such a gas provides 1-10 percent Cl₂ and about 1.5 percent S₂Cl₂, based on the catalysts. A "saturated" mixture of CCl₄ and Cl₂ or HCl can be made by bubbling chlorine or hydrogen chloride gas at room temperature through a vessel containing CCl₄; such a mixture generally contains about 1 part CCl₄:5-10 parts Cl₂ or HCl. Conveniently, a pressure of about 0-100 or more p.s.i.g., preferably about 0-15 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 the sulfate or other water-dispersible form is described in copending applications Serial No. 763,834, filed September 29, 1958, and Serial No. 842,618, filed September 28, 1959, and may be accomplished, for instance, 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 includes sulfiding the catalyst and converting the sulfide by an oxidation process, after which metal contaminants in water-dispersible form, preferably prior to an ammonium wash may be dissolved 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 the sulfate or other water-soluble 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 convert metal sulfide to sulfate, including oxysulfate, or other water-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 atmospheres 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 converted to the corresponding sulfate, or other water-dispersible form, by a liquid aqueous oxidizing agent such as a dilute hydrogen peroxide or hypochlorous acid water solution, as described in copending application Serial No. 842,618, filed September 28, 1959. 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, enough extra sulfuric or nitric acid may be used to provide one mole of sulfate or two moles of nitrate for each two moles of sodium or potassium.

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 five 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 oxidize the sulfides to sulfate or other 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 super-atmospheric 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 metal sulfate, nitrate, etc. 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 justify 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 and some iron may be removed through conversion of the nickel sulfide to the volatile nickel carbonyl by treatment with carbon monoxide, as described in copending application Serial No. 47,598, filed August 5, 1960. 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. Some iron contaminant is also removed by this carbonylation treatment.

Hydrogenation takes place at a temperature of about 800 to 1600° F., at a pressure from atmospheric 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 50-100 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 100-180° F. The CO treatment serves generally both to convert the elemental metals, especially nickel and iron 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 accompanying drawing which shows the schematic of a representative processing system, but is not to be construed as limiting.

A feed contaminated with poisoning metals and which is to be improved in its hydrogen-to-carbon ratio is fed by line 10 to the hydrotreater 12, a vessel containing a hydrogenation catalyst. The hydrotreater illustrated may be one of a plurality of such vessels used in parallel. Such an arrangement provides for withdrawal of a unit from hydrotreating when regeneration of the catalyst is required without taking other units off stream. For purposes of regeneration the hydrotreater 12 is provided with a source 14 for regenerating gas, e.g., air and with a means 16 to exhaust flue gases. The feed, for instance, a heavy gas oil preferably flows downwardly through the bed of catalyst along with hydrogen from the pipe 18. This hydrogen may come from the external source 20 or be recycled from the hydrotreater effluent by line 22. Conditions in the hydrotreater are maintained as described above and the effluent is removed by the line 24 to the flash drum 26 for separation of free hydrogen from the effluent.

The remaining portion of the effluent is conducted by line 28 to fractionator 30. The fractionator separates from other materials of the hydrotreater effluent, the portion suitable as a feedstock for catalytic cracking which can be all or a part of the hydrotreated product. This is withdrawn from the fractionator by line 32. Other portions of the hydrotreater effluent which are not sent to the catalytic cracker may be separately withdrawn from the fractionator as by the line 34 for fixed gases, 36 for gasoline components and 38 for heavy residual-type components. These latter components may be withdrawn from the system by line 40 or may be sent to the catalytic cracker by line 41 or recycled to the hydrotreater by lines 42 and 44.

The cracker feedstock and fluid cracking catalyst are brought to the cracker 46 by the line 48 along with any additional cracking feed components from line 49. The cracker may be provided with the cyclone separator 50 to disentrain catalyst fines from the cracker effluent which leaves by line 52. This effluent is brought to fractionator 54 where components of the effluent are withdrawn by line 56 for fixed gases, line 58 for gasoline, line 60 for gas oil components and line 62 for materials higher boiling than gas oil. The latter components may be withdrawn from the system by line 64, or may be recycled by lines 66, 68, 70 and 72 to the hydrotreating zone along with gas oil components from the cracker effluent from the line 60 if desired.

Preferably the gas oil fraction in the cracker effluent is recycled to the catalyst cracking step by lines 74 and 48, since it is substantially poison free and since its hydrogen-to-carbon ratio does not need too much improvement.

Contaminated catalyst is continuously removed from the cracker 46 by the standpipe 76 whence it is conducted, for example, by air from the source 78 to the regenerator 80 by the pipe 82. The regenerator is provided with the exit 84 for exhaust gases and with the standpipe 86 for removal of regenerated catalyst. This is returned to the cracker by the pipes 74 and 48. As illustrated one of the feed materials to the cracker, in this case cycle oil, may be used to convey the catalyst particles.

A small slip-stream of catalyst may be removed from the standpipe 86 for demetallization. The drawing illustrates a demetallization system which includes apparatus for sulfiding, chlorinating, washing and filtering the catalyst. Pipes 88 and 90 conduct the catalyst to an outer chamber 92 of the sulfider 94 where the catalyst may be preheated before entering the main chamber through opening 96. In the sulfider the catalyst passes counter-

currently as a fluidized bed to sulfiding vapors entering by line 98. Catalyst exits by line 100 and waste sulfiding gas exits by line 102. Line 100 brings the catalyst to chlorinator 104 where it passes countercurrent to chlorinating vapor entering from line 106. Exhaust chlorinating vapor and vaporized metal poisons leave by line 108 and catalyst, reduced in vanadium and/or iron content passes by line 110 to slurry tank 112 which is kept supplied with water, perhaps containing pH-adjusting components, from the line 114. Agitation is maintained in the slurry tank by suitable means (not shown) and the slurry is quickly withdrawn by line 116 to the filter 118. 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 120 and scraped from the filter by doctor blade 122. Excess aqueous material is removed from the system by line 124. Catalyst goes by route 126 to wash tank 128. A slurry of catalyst in wash water may be brought by line 130 back to regenerator 80.

Means are generally provided for including a second feedstock in part or all of the processing system of this invention. Such a second feed may be an unpoisoned stock, such as a light gas oil, which may be added from source 132 to the hydrotreater feed by line 134 or to the cracker feed by line 49.

As an example of the treating process of this invention, 17,000 barrels per day of a vacuum gas oil boiling in the range of about 800 to 1100° F. and derived from a Mid-Continent crude are fed, along with 5000 barrels/day of a cycle oil from a later cracking stage to a hydro-treating operation. The gas oil contains about 0.8 p.p.m. NiO and about 1.5 p.p.m. V_2O_5 .

In the hydrotreater the conditions maintained are about 725° F., about 500 p.s.i.g., about 1 WHSV and 300 standard cubic feet of hydrogen per barrel of gas oil charged. The reaction is conducted in the vapor phase. About 250 standard cubic feet of hydrogen per barrel of total gas oil are consumed in the hydrotreater. The product of the hydrotreater is taken to a flash drum operated at about 450 p.s.i.g., and hydrogen-containing gases are removed for recycle. The liquid product issuing from the flash drum is about 22,000 barrels per day and boiling between about 400 to 1100° F. The hydrotreater effluent contains about 0.2 p.p.m., NiO and 0.4 p.p.m. V_2O_5 .

In the catalytic cracker the gas oil feed contacts a synthetic-gel silica-alumina catalyst, having an Al_2O_3 content of about 25%, at a temperature of about 950 to 975° F. and a pressure of about 5 p.s.i.g. The cracked products are introduced to a fractionator where a 75% yield of gasoline and other components are removed. The cycle gas oil can be recycled to the cracker for further processing. A portion of the silica-alumina catalyst is continuously removed from the cracking reactor and brought to a regenerator. Average residence time in the regenerator is about 5 minutes at a temperature of about 1100° F. before returning to the reactor at a carbon level of less than about 0.5%.

About 10% per day of the cracking catalyst inventory poisoned to a metals level of about 30 p.p.m. NiO, 115 p.p.m., vanadium and 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. Water containing dilute hydrogen peroxide mixed with nitric acid is brought in contact with the sulfided catalyst for about 10 minutes at a temperature of 200° F. 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 iron, nickel and vanadium content is filtered from the wash slurry, dried at about 350° F. and returned to the regenerator. The treated catalyst is analyzed and shows a metals content of 12 p.p.m. nickel, and 85 p.p.m. vanadium.

In another operation 10,000 barrels per day of a vacuum residuum boiling above about 1000° F. are fed, along with 5,000 b./d. of a cycle oil from a later cracking stage to a hydro treating operation as a mixture of liquid and vapors. The residuum contains about 21.3 p.p.m. nickel oxide and 122 p.p.m. vanadium measured as V_2O_5 . The hydrotreater contains a fixed bed of cobalt-molybdena-alumina catalyst analyzing about 2.5% Co and 9% MoO_3 . In the hydrotreater the conditions maintained are about 800–850° F., about 1500 p.s.i.g., about 1 WHSV and 6000 standard cubic feet of hydrogen per barrel of total feed charged. About 1000 standard cubic feet of hydrogen per barrel of feed are consumed in the hydrotreater which converts about 75% of the residuum charge to lower boiling materials. The product of the hydrotreater is taken to a flash drum operated at about 1450 p.s.i.g. and the hydrogen-containing gases are removed for recycle. The liquid product issuing from the flash drum is blended with half its volume of a substantially metal free cycle oil from the cracker effluent to provide about 15,000 b./d. of a cracking feedstock containing about 2.9 p.p.m. Ni and 7.9 p.p.m. V.

In the catalytic cracker the feedstock contacts a synthetic-gel silica-alumina catalyst, having an Al_2O_3 content of about 25%, at a temperature of about 950 to 975° F. and a pressure of about 5 p.s.i.g. The cracked products are introduced to a fractionator where a 75% yield of gasoline and other low-boiling components are removed. The residue, including gas-oil fractions is recycled to the hydrotreater for further processing. A portion of the silica-alumina catalyst is continuously removed from the cracking reactor and brought to a regenerator. Average residence time in the regenerator is about 5 minutes at a temperature of about 1100° F., before returning to the reactor at a carbon level of about 0.4%.

About 30% of the cracking catalyst inventory poisoned to a metals level of about 155 p.p.m. nickel, and 930 p.p.m. vanadium 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 an hour. The catalyst is then purged with flue gas at a temperature of about 575° F. and chlorinated in a chlorination zone with an equimolar mixture of Cl_2 and CCl_4 at about 600° F. After about 1 hour no trace of iron or vanadium chloride can be found in the chlorination effluent and the catalyst is quickly washed with water. A pH of about 2 is imparted to this wash medium by chlorine entrained in the catalyst and the wash serves to remove nickel chloride. The demetallization procedure removes about 60% of the nickel and about 25% of the vanadium on the catalyst.

Other runs were made using the same hydrotreater feed by varying the pressure in the hydrotreater. When 500 p.s.i.g. was employed, the hydrotreater effluent contained 5.3 p.p.m. Ni and 18.7 p.p.m. V. When 2500 p.s.i.g. was used, the effluent contained 2.3 p.p.m. Ni and 4.7 p.p.m. V.

Thus, while hydrotreating alone is frequently not sufficient to prevent poisoning with metals a catalyst used in a later cracking of a feedstock, this invention provides for overcoming poisoning effects by a balanced process which includes hydrotreating and cracking catalyst demetallization.

We claim:

1. In a method for converting to gasoline mineral hydrocarbon oil boiling above the gasoline range, the steps consisting essentially of hydrotreating the mineral hydrocarbon oil containing at least about 0.5 p.p.m. nickel and at least about 0.5 p.p.m. vanadium in the presence of a hydrogenation catalyst and molecular hydrogen at an elevated temperature of about 600 to 900° F. and superatmospheric pressure to reduce partially the con-

tent of said contaminating metal by about 10 to 90% while consuming hydrogen and increasing the hydrogen-to-carbon ratio, contacting resulting hydrocarbon product boiling above the gasoline range and containing at least about 0.1 p.p.m. nickel and at least about 0.3 p.p.m. vanadium with a solid silica-based cracking catalyst under cracking conditions in a cracking zone to produce a conversion of about 40 to 70% to products boiling in the gasoline range, passing catalyst from the cracking zone to a regeneration zone wherein carbon is burned from the catalyst, passing regenerated catalyst to the cracking zone, withdrawing from the cracking-regeneration system contaminated catalyst containing at least about 50 p.p.m. nickel and at least about 50 p.p.m. vanadium, demetallizing withdrawn catalyst to remove about 10 to 90% of said metal impurities and returning demetallized catalyst to the cracking system.

2. The method of claim 1 in which catalyst demetallization includes contact of the catalyst with a vapor reactive with metal contaminant.

3. The method of claim 1 in which the cracking catalyst is a synthetic silica gel catalyst.

4. The method of claim 1 wherein the initial hydrocarbon fraction containing contaminating metal boils in the range of about 400 to 1200° F.

5. The process of claim 1 wherein the hydrocarbon product of from the hydrotreating contains about 50 to 90 weight percent less metal contaminants than the hydrocarbon oil charged to said hydrotreating.

6. The method of claim 1 wherein the catalyst is demetallized by contacting the catalyst with a molecular oxygen-containing gas at a temperature of about 1150 to about 1600 F., sulfiding the poisoning metal containing component on the catalyst by contact with a sulfiding agent at a temperature of about 800 to 1500 F., chlorinating poisoning metal containing component on the catalyst by contact with an essentially anhydrous chlorinating agent at a temperature of about 300 to 1000° F., removing poisoning metal chloride in vapor form from the catalyst, contacting the catalyst with a liquid, essentially aqueous medium to remove soluble poisoning metal chloride from the catalyst.

7. The method of claim 6 in which the sulfiding is performed by contact with H₂S.

8. The method of claim 6 in which the chlorinating is performed with an equimolar mixture of Cl₂ and CCl₄.

9. The method of claim 6 wherein the hydrocarbon product from the hydrotreating contains about 50 to 90 weight percent less metal contaminants than the hydrocarbon oil charged to said hydrotreating.

10. In a method for converting to gasoline mineral hydrocarbon distillate oil boiling in the gas oil range, the steps consisting essentially of hydrotreating the mineral hydrocarbon oil containing about 0.5 to 3 p.p.m. nickel and about 0.5 to 10 p.p.m. vanadium in the presence of a hydrogenation catalyst and molecular hydrogen at an elevated temperature of about 600 to 900° F. and superatmospheric pressure to reduce partially the content of said contaminating metal by at least about 50 to 90% while consuming hydrogen and increasing the hydrogen-to-carbon ratio, contacting resulting hydrocarbon product boiling above the gasoline range and containing at least about 0.1 p.p.m. nickel and at least about 0.3 p.p.m. vanadium with a fluidized, synthetic gel, silica-alumina cracking catalyst under cracking conditions in a cracking zone to produce a conversion of about 40 to 70% to produce boiling in the gasoline range, passing catalyst from the cracking zone to a regeneration zone wherein carbon is burned from the catalyst, passing regenerated catalyst to the cracking zone, withdrawing contaminated catalyst from the cracking-regeneration system at a rate of about 5 to 50% per day of the catalyst in the cracking-regeneration system, the withdrawn contaminated catalyst containing at least about

50 p.p.m. nickel and at least about 50 p.p.m. vanadium, demetallizing withdrawn catalyst to remove about 60 to 90% of the nickel and about 20 to 40% of the vanadium, and returning demetallized catalyst to the cracking system.

11. In a method for converting to gasoline mineral hydrocarbon residual oil boiling above the gasoline range, the steps consisting essentially of hydrotreating the mineral hydrocarbon oil containing more than about 1 p.p.m. nickel and more than about 1 p.p.m. vanadium in the presence of a hydrogenation catalyst and molecular hydrogen at an elevated temperature of about 600 to 900° F. and superatmospheric pressure to reduce partially the content of said contaminating metal by at least about 50 to 90 percent while consuming hydrogen and increasing the hydrogen-to-carbon ratio, contacting resulting hydrocarbon product boiling above the gasoline range and containing at least about 0.2 to 10 p.p.m. nickel and at least about 0.5 to 20 p.p.m. vanadium with a fluidized, synthetic gel, silica-alumina cracking catalyst under cracking conditions in a cracking zone to produce a conversion of about 40 to 70 percent to products boiling in the gasoline range, passing catalyst from the cracking zone to a regeneration zone wherein carbon is burned from the catalyst, passing regenerated catalyst to the cracking zone, withdrawing contaminated catalyst from the cracking-regeneration system at a rate of about 5 to 50 percent per day of the catalyst in the cracking-regeneration system, the withdrawn contaminated catalyst containing at least about 155 p.p.m. nickel and at least about 500 p.p.m. vanadium, demetallizing withdrawn catalyst to remove about 60 to 90 percent of the nickel and about 20 to 40 percent of the vanadium and returning demetallized catalyst to the cracking system.

12. In a method for converting to gasoline mineral hydrocarbon residual oil boiling above the gasoline range, the steps consisting essentially of hydrotreating the mineral hydrocarbon oil containing more than about 1 p.p.m. nickel and more than about 1 p.p.m. vanadium in the presence of a hydrogenation catalyst and molecular hydrogen at an elevated temperature of about 600 to 900° F. and superatmospheric pressure to reduce partially the content of said contaminating metal by at least about 50 to 90 percent while consuming hydrogen and increasing the hydrogen-to-carbon ratio, contacting resulting hydrocarbon product boiling above the gasoline range and containing at least about 0.2 to 10 p.p.m. nickel and at least about 0.5 to 20 p.p.m. vanadium with a fluidized, synthetic gel, silica-alumina cracking catalyst under cracking conditions in a cracking zone to produce a conversion of about 40 to 70 percent to products boiling in the gasoline range, passing catalyst from the cracking zone to a regeneration zone wherein carbon is burned from the catalyst, passing regenerated catalyst to the cracking zone, withdrawing contaminated catalyst from the cracking-regeneration system at a rate of about 5 to 50 percent per day of the catalyst in the cracking-regeneration system, the withdrawn contaminated catalyst containing at least about 155 p.p.m. nickel and at least about 500 p.p.m. vanadium, demetallizing withdrawn catalyst to remove about 60 to 90% of the nickel and about 20 to 40 percent of the vanadium by contacting the catalyst with a molecular oxygen-containing gas at a temperature of about 1150 to about 1600° F., sulfiding the poisoning metal-containing component in the catalyst by contact with a sulfiding agent at a temperature of about 800 to 1500° F., chlorinating poisoning metal-containing component on the catalyst by contact with an essentially anhydrous chlorinating agent at a temperature of about 300 to 1000° F., removing poisoning metal chloride in vapor form from the catalyst, contacting the catalyst with a liquid, essentially aqueous medium to remove soluble poisoning metal chloride from the catalyst.

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13. The method of claim 12 in which the sulfiding is performed by contact with H_2S and the chlorinating is performed by contact with an equimolar mixture of Cl_2 and CCl_4 .

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