PRETREATMENT AND CRACKING OF RESIDUAL OILS

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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 a crude oil which contains metal poisons and pretreat them prior to cracking in order that the cracking operation itself becomes more trouble-free overall even though pretreatment adds to the cost and may sometimes reduce the amount of cracking feed per barrel of crude and thereby diminish the yield of gasoline or be inefficient in moving metal poisons, especially from a residuum. Although the cracking catalyst employed can be discarded 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.

Attempts to employ heavier fractions of crude oil for catalytic cracking have been limited heretofore due to the presence of metal contaminants in such heavy fractions. The highest boiling fractions of a crude oil contain substantial portions of metal contaminants, particularly nickel and vanadium. When an attempt is made to segregate higher boiling distillate fractions of a crude oil, some portion of these metal contaminants and coke-formers is inherently and unavoidably carried over into the distillate product. For example, when a heavy gas oil distillate fraction, having a boiling range of about 300° to 1100° F., is segregated from a crude oil, about 0.1 to 1 pound per 1000 barrels of metal contaminants sometimes can be obtained from the gas oil distillate in a typical distillation.

The problem of metal contaminant carryover in the segregation of heavy distillate fractions is believed to be due to two phenomena. First of all, it is believed that the metal contaminants occur or are converted during distillation to the form of metal complexes. These complexes may generally be identified as large condensed ring substances. Some of these metal complexes and particularly nickel porphyrins are sufficiently volatile so as to be carried overhead under vacuum distillation conditions. Consequently, when attempting to segregate heavy boiling gas oil fractions including components boiling above about 700 or 900° F., volatile metal contaminants are unavoidably obtained in the distillate product. The second phenomenon is generally referred to as mechanical entrainment. In distillation a small portion of high boiling liquid hydrocarbons from the residual fraction is normally entrained in the lower-boiling components taken overhead in a distillation operation. Since liquid hydrocarbons derived from residuals contain concentrated amounts of metal contaminants, such entrainment in distillate products accounts for a portion of the metal contamination of such distillates.

Since essentially fewer metals are found in most petroleum distillates which boil below about 700 or 900° F., petroleum refiners are frequently limited to cracking stocks in this lower boiling range recoverable from a crude source by distillation at atmospheric or slightly reduced pressures. The metal poisons and coke-formers are for the
most part left behind in the non-distilled, residue portion of the oil. Refiners, therefore, are usually provided with a distillation point of the crude, which is relatively low, in metals and coke formers to serve as feed to catalytic cracking. However, there is available in most crudes a considerable amount of oil, boiling in the range of about 700 to 1200° F. or higher, which would be a good cracking stock if it could be recovered sufficiently free of metal poisons and coke formers. Yet, vacuum distillation of the highly metals-contaminated residual frequently carries a good deal of metals over into the heavy gas oil distillate thereby obtained. In this invention the metals content of the feedstock is reduced by hydrogenation prior to the vacuum distillation, offering higher boiling components less contaminated with metals and coke-formers which are subject to volatilization and/or entrainment in the vacuum distillation.

It has been proposed heretofore to hydrogenate 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, and 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 and the amount of hydrogen consumed. High severity can increase the extent of metals removal; however, it may involve a greater consumption of hydrogen, a larger capital investment for high-pressure equipment, and a reduction in the yield of cracking feedstock.

Petroleum fractions containing large amounts of coke-forming and/or metal components, such as the asphaltic and residual materials described above, frequently require such severe hydrotreating to make them trouble-free cracking feeds in conventional processes that the expense of such hydrotreating is not practical. This invention employs partial demetallizing of a cracking feed by hydrogenation and distillation along with demetallization of the cracking catalyst by procedures to be described, to achieve greater economy than would be obtained by employing only one of the demetallizing techniques: hydrogenation and/or distillation on the one hand, or poison removal and the cracking catalyst on the other hand, in the attempt to obviate poisoning effects. In the operation of this invention, hydrogenation, distillation and catalytic cracking of heavier mineral hydrocarbon oil feedstocks to produce gasoline are combined and balanced with a procedure for reducing poisoning metals on the cracking catalyst to present a much more attractive alternative to the individual operations described above for overcoming an overall metals problem. Under these conditions all four of the hydrogenation, distillation, 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 and the vacuum distillation less likely to produce a heavy gas oil too contaminated for use in cracking. In this method the metal-containing hydrocarbon feedstock is hydrogenated under conditions giving a desired hydrogenation effect with partial, but not complete, removal of poisoning metals. The hydrogenated oil or a selected portion thereof boiling above about 400° F. and containing a significant amount of metal content is obtained to obtain a heavy gas oil fraction, containing substantially less contaminants than the hydrogenated product, which is then catalytically cracked by itself or after blending with conventional cracking feeds 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 reaction. As a result of this hydrogenation 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 charge, i.e., a given cracking capacity. The cracking aspect of this invention in combination with its demetallization features is economically attractive when a cracking feedstock is contained obtaining as little as about 0.5 p.p.m. nickel and or about 0.5 p.p.m. vanadium.

The feed to the present process comprises 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 residual feedstock will usually include at least about 5 or 10 weight percent of heavy metals. These are materials generally avoided for use as catalytic 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. Residua containing metals in these generally undesirable ranges are the oils which this invention salvages. Residua containing metals in these generally undesirable ranges are the oils which this invention salvages. Residua containing metals in these generally undesirable ranges are the oils which this invention salvages. This invention has a number of effects. One use is to dissociate the heavy poisoning metals from their compounds in the feedstock. Hydrogenation also serves to saturate components of the feedstock. Also, hydrogenation may cause a certain amount of the feed to be converted (cracked) to lower boiling materials. This factor may sometimes make residual oils a more desirable feedstock for this invention than lower boiling materials of the same metal content. Since more cracking is not only permissible but indeed sometimes desirable when hydrogenation is performed on a residual to prepare it for catalytic cracking, the hydrogenation may be performed at higher temperatures. At these temperatures, hydrogenation can perform its demetallization and saturation functions at a lower pressure, thereby lowering equipment costs. Any gas or gasoline produced in the hydrogenation and unsuitable for use as feed to the catalytic cracking may be used as reformer feedstock, although hydrogenation of residuals usually does not produce overly large amounts of these materials. Usually greater than about 10% of the residual hydrocarbon charge may be converted to boiling normally liquid materials by hydrogenation and quite frequently at least about 25% is converted. Conversion to lower boiling materials rarely exceeds 80% of a residual charge.

In the hydrogenation operation hydrogen is consumed...
by chemical combination with a component of the hydrocarbon feed. Where hydrocracking is performed the hydrogen consumption will be high, as in the case of treating most residual hydrocarbon oils. Hydrogenation optimizes modifications from which the petroleum refiner may choose, depending upon the residual stock to be treated and the results desired. Hydrogenation may be performed by free or molecular hydrogen in the presence of a catalyst or by a hydrogen donating chemical with or without a catalyst. Elevated temperature (about 400°-1200° F.) and/or pressure (atmospheric to 3000 p.s.i.g.) conditions usually prevail in hydrogenation, and within these ranges conditions can be chosen to give the desired degree of oil demetallization,saturation and/or cracking.

Hydrogen donor diluent cracking (HDDC) is widely known in the art and is illustrated in abandoned application Serial No. 365,335, filed July 1, 1953, by Arthur W. Langner, Jr. as disclosed in U.S. Patent 2,772,718. The donor diluent is a material, generally a hydrocarbon, which has the ability to take up hydrogen in a hydrogenation zone and readily release it in a thermal treating zone. It is believed that the donor diluent operates by yielding hydrogen atoms to the radicals that have been created from the residuum by the thermal treatment, thereby upgrading the residuum and preventing condensation and/or polymerization of the radicals.

In donor diluent processes, the donor diluent material must be substantially unaltered as it passes through the process, and it is usually customary to recycle the material so that it is used over and over again as a hydrogen carrier. Donor materials may be added as a relatively pure chemical substance such as tertalin or Decalin, or in admixture with other materials, particularly hydrocarbons, or the donor diluent may be a partially hydrogenated catalytic cycle oil, a partially hydrogenated lubricating oil extract or other partially hydrogenated aromatic. Hydrogen donor materials usually contain condensed ring aromatics in sufficient quantities to serve as a hydrogen carrier. These aromatics are partially hydrogenated; there is added to them some easily removable hydrogen atoms, but not enough to convert the aromatics substantially to naphthenes. This material after being partially hydrogenated, can be admixed with the feedstock in the process and the mixture thermally treated, whereupon the hydrogen is transferred from the partially hydrogenated material to the hydrogen-deficient residuum.

After blending of hydrogen donor diluent and residuum, the blend is then taken to a thermal or catalytic cracking zone to decompose the residuum into gas, liquid and volatile oils from the cracker, fractional distillation of this process may also be added. The mixture of residual and diluent may be thermally cracked by heating to a temperature of about 700 to 1200° F., preferably about 800 to 1000° F. at pressures within the range of from about atmospheric to about 2000 p.s.i.g. preferably from about atmospheric to about 200 p.s.i.g. with a holding time of about 5 to 30 minutes. A conventional coil or coil and drum heater may be used. A wide range of conversion may be obtained by varying the temperature or feed rate in the thermal cracking operation depending upon the feed to be processed, to produce from about 40 to 80 percent converting lower boiling materials per pass. The weight ratio of diluent to residual plus recycle bottoms is usually between about 0.1/1 to about 10/1, preferably about 0.5 to 2/1. A high rate of diluent to feed and a moderately high hydrogen content tend to reduce the formation of metal contaminants at any severity. However, the severity of thermal cracking is primarily a function of cracking temperature and feed rate. The nature of the residual and its prior processing, if any, may affect the cracking severity and the amount of metal removal.

In the catalytic donor cracking method (CDC) a petroleum residuum can be contacted at elevated temperatures with an essentially anhydrous catalyst comprising the hydride of a halogen having an atomic number of 35 to 53 and in the presence of a hydroaromatic material. As a result, valuable low molecular weight hydrocarbon gases primarily boiling below C6 and gasoline having an end boiling point of about 430° F. are produced along with a good yield of gas oils which form catalytic cracking stock, and a residual oil boiling primarily above 950° F. which is reduced in containing metals. The catalyst in this process is hydrogen iodide or hydrogen bromide. These can be added as such to the reaction zone or the corresponding elemental halogen, that is, bromine or iodine, or other material which gives the halogen hydride may be charged. The halogen hydride is apparently in equilibrium in the reaction zone with elemental halogen. The halogen hydride may predominate in the equilibrium mixture. The catalyst selected is employed in a substantially anhydrous form although it may be used in solution with alcohol or other solvents. The amount of catalyst utilized normally depends on the characteristics of the residual treated, for instance, the type and amount of metal contaminants, and the amount of nitrogen, sulfur, etc. present. The amount of catalyst employed is generally from about 0.01 to 5 percent by weight of the residual treated with a preferred amount being about 0.1 to 2 percent.

The hydrogen donor can be contacted with the residual oil to be treated in any suitable manner. The donor may be added to the oil prior or subsequent to the addition of the catalyst to the oil. The amount of hydroaromatic compound employed is generally at least about 20% of the residual feed and usually is in a range of from about 50 to 200 percent by weight of the oil treated. The hydroaromatic material is a liquid at the conditions of the process and acts as a hydrogen donor as described above. When added in admixture with other hydrocarbons, the hydroaromatic is usually at least about 40 or 50%, preferably at least about 75% of the mixture. During the CDC treatment the temperature is usually in the range of about 700 to 1200° F. with a preferred temperature being about 750-850° F. The pressure may vary widely depending on the particular feedstock undergoing treatment and the temperature employed, but it is essential that substantial cracking and conversion to lower boiling oils occurs. The pressures will generally be elevated and vary from about atmospheric to 2000 p.s.i.g. with a preferred range being from about 500 to 1500 p.s.i.g. The addition of free hydrogen in the CDC process is normally advantageous as it can increase the liquid product yield and aid in the hydrocracking. Under normal operating conditions it may be desirable to employ hydrogen, preferably at a partial pressure of at least about 100 p.s.i.g. There does not appear to be any particular benefit in providing a hydrogen partial pressure in excess of about 1500 p.s.i.g., the preferred pressure being from about 300 to about 1000 p.s.i.g. Hydrogen consumption will usually be no more than about 1000 standard cubic feet per barrel of residuum treated. This process allows for a conversion of at least about 20% of the feedstock to a liquid material boiling below about 950° F.

Hydrogenation of the residual using free hydrogen and a catalyst may be conducted by contacting the petroleum feed with the catalyst in the presence of free hydrogen under superatmospheric pressure. The hydrogenation catalysts generally known in the art can be employed for this purpose. A specific solid hydrogenation catalysts are preferred and they are usually disposed as a fixed bed of macroporous particles, say of about 1/16" to 1/4" in diameter and about 1/16" to 1" or more in length. A moving bed of macroporous catalyst or a fluidized bed of finely divided catalyst can also be used. The catalyst contains catalytically active amount of a hydronation 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 iron group, molybdenum, tungsten and combinations thereof. Frequently the metals are disposed as inorganic compo-
ments, 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 VI of the periodic chart having atomic numbers from 47 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 catalyst 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% and preferably at least about 2%, of each catalytically active metal when combinations are used.

Catalytic hydrogenation 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. may be employed and the pressures are generally superatmospheric usually falling in the range of about 300 to 3000 p.s.i.g. Freo or molecular hydrogen may be 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 while in the area of about 0.1 to 10 or more. (weight of hydrocarbon feedstock per hour per weight of catalyst). 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 in the range of about 1000 to 2000 or more on a standard cubic feet per barrel. Residual oils are often treated at about 750 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 1,000 standard cubic feet of hydrogen per barrel. The treatment of residual material under non-cracking conditions in the presence of catalytic material and hydrogen or a hydrogen donor is conducted under suitable temperature and pressure conditions so that there is not a substantial amount of cracking, i.e., less than about 15 weight percent of the petroleum feedstock, preferably less than about 5% is cracked. The treating temperature will usually be in the range of about 400 to 700° F., with about 600 to 700° F. being most suitable. The total pressure in the reactor is usually at least about 100 p.s.i.g., more often at least about 300 p.s.i.g., and no reason has been seen for going above about 3000 p.s.i.g. Preferably the pressure will be in the range of about 1500 to 2000 p.s.i.g. It is preferred not to introduce free hydrogen into the system when treating residuals with a hydrogen donor diluent because the added hydrogen is not consumed efficiently. However, when free hydrogen is introduced into the system the hydrogen partial pressure is about 100-2000 or 3000 p.s.i.g., preferably about 200-500 p.s.i.g. The length of time of the treatment may vary widely so long as conversion of the petroleum feed is limited as noted before. The treatment may take from about 0.5 to 3 hours and, of course, lower temperatures may require longer contact times to obtain a given result.

As in HDC, the hydroaromatic compound can be contacted with the hydrocarbon oil to be treated in any suitable manner in the proportions recited. When treating residuals the hydrogen donor material is preferably low boiling so that it may be separated overhead by distillation from the product at atmospheric or slightly reduced pressures. Since substantial cracking is avoided in this hydrogenation operation the lighter donor is readily recovered since it will not be unduly contaminated with light gas oil. The catalyst in the non-cracking process is contacted with the substantially hydrogen iodide which can be added as much as such to the reaction zone or iodine or another hydrogen iodide-producing material may be added. In any event, the hydrogen iodide is apparently in equilibrium with elemental iodine in the reaction zone although the catalyst may be predominantly hydrogen iodide. The catalyst can be contacted with the petroleum feedstock in any convenient manner and the catalyst is essentially in anhydrous form although it may be used in solution with alcohol or other solvents. The amount of catalyst used can depend upon the reaction conditions and the amount of feedstock demetallization required, but is generally from about 0.1 to 20% of the oil to be hydrorefined, preferably about 1 to 10%.

After the hydrogenation the hydrogenated product material may be fractionated usually at atmospheric pressure to obtain gaseous hydrocarbons, gasoline, a diluent cut and heavy bottoms comprising the entire oil fraction and material boiling above a given temperature. The gasoline fraction may be hydrotreated, thereby increasing its octane rating. The diluent cut is separated from other portions of the hydrorefiner effluent and hydrorefined to increase its hydrogen content. After distillation, the residuum is generally in the presence of a solid catalyst as described above.

The entire hydrogenated bottoms product described above may be charged to a vacuum distillation unit, but it is preferable from the standpoint of economy in the process of this invention to remove in a distillation at atmospheric or slightly reduced pressure the substantially metals-free gas oil fraction boiling essentially in the range of about 400 to 700 or 900° F., which is amenable to direct catalytic cracking from the bottoms which have a boiling point in the range above about 700 to 900° F. before vacuum distillation and conduct it directly to the residuum boiling in the range of about 1000 to 2000 or more. The vacuum distillation is generally in the range of about 1050 to 1100° F. (corrected to atmospheric pressure) and reduced in metal contaminant content. The contaminated residue asphalt fraction from this vacuum distillation generally boils primarily above about 1050 or 1100° F. and may be put to low value uses, such as heating oils or road surface materials.

Hydrogenation gives a partial reduction in metals content of the residuum. The metals remaining in the hydrogenated product would accumulate on the 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 hydrogenating step and severely reducing the yield of gasoline in the cracker effluent. In this invention hydrogenation may remove only about 10% of the metals. Frequently the reduction of one or all of nickel, vanadium and iron will be about 65 to 90 weight percent. The hydrogenated product contains at least about 2 p.p.m. nickel and/or about 3 p.p.m. vanadium, more usually about 25 to 50 p.p.m. total nickel and vanadium, but rarely more than 150 p.p.m.

Hydrogenation usually does not remove metal contaminants to a point that is insignificant in subsequent catalytic cracking. The hydrorefined product also may contain some hydrocarbon constituents which are unsuitable for inclusion in a catalytic cracking feedstock. However, by subjecting the heavy constituents in the hydrorefiner effluent to vacuum distillation a very deep cut of heavy gas oil is obtained which is reduced in metals and coke formers and therefore suitable as a catalytic cracking feedstock.

The residue from the vacuum tower, containing substantial amounts of all the metal contaminants that were present in the hydrogenated product or fraction thereof, may be removed from the system or recycled back to the hydrorefiner unit. Temperature and pressure conditions are adjusted to secure the proper distillation of the hydrogenated product or portion thereof. Thus, the
3,162,596 temperature in the vacuum tower will be about 700 to 775 °F. and the pressure will usually be in the range of about 10 to 30 mm. Hg. Steam may be introduced into the vacuum tower to further reduce the partial pressure of the hydrocarbons. The gas oil feed would normally be in the condensing point between about 700 to 1100 °F. and amounting to about 50 to 85% by weight of the hydrogenated material fed to the vacuum distillation is then used as a feedstock to the catalytic cracking operation. As much as about 90%, preferably about 70 to 80% of the metal content of the gas oil, such as nickel and vanadium, of the hydrogenated product or portion thereof fed to vacuum distillation are left in the vacuum tower residue. In the practice of this invention the gas oil fraction from the vacuum tower may often contain about 1–5 p.p.m. nickel and/or about 1 to 10 p.p.m. vanadium calculated as the common oxide. The use of a catalyst demetallization unit with the catalytic cracker counteracts the remaining metals content, thereby enabling much deeper cuts of the residual feed to be brought to the hydrogenation, much deeper cuts of hydrogenated effluent distillate to be sent to catalytic cracking without vacuum distillation and a much deeper cut of the hydrogenated effluent, and residue; a slightly higher metals content in the vacuum gas oil being rendered acceptable by catalytic demetallization.

Contaminating metals in greater quantities than are acceptable to the art generally are present in the cracker feedstock, which boils above the gasoline range, preferably in the range of about 400 to 1100 or 1200 °F. and contains a significant amount of the vacuum gas oil fraction. The amount of this product in the cracking feed will be at least about 5–10% preferably about 20–50%. The remaining portion of the cracker feed may comprise cracking feeds of more or less conventional types, that is, virgin gas oils, atmospherically distilled hydrogenator effluent, etc. The cracking feed component proportions will be adjusted to provide a feed containing more than about 0.5 p.p.m. nickel and/or 0.5 p.p.m. vanadium and preferably the total feed to cracking will contain less than about 4 p.p.m. nickel and/or 8 p.p.m. vanadium. At least about 0.5 p.p.m. nickel and/or about 0.5 p.p.m. vanadium is contributed to the cracker feed by the vacuum gas oil.

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 a batch semi-continuous process 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, 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. In a highly preferred form of this invention is a fluidized (fluidized) catalyst, for instance, having particles predominately 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.

Vaporized 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 results in a bottom product containing 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, as fixed gases, boiling below the gasoline range are removed from the system. Bottoms, that is, those products boiling below the gasoline range conveniently are recycled to the hydro-treating or catalytic cracking zones by blending with them with virgin residue feed and/or hydrogenated product. 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 bed oil cracking unit 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 the 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 1/4%. The regeneration of any particular quantity of catalyst is generally regulated to give a carbon content in the coke 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 hydrogenation step and severely reducing the yield of gasoline in the cracker effluent.

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 plant'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. of nickel, preferably more than 50 p.p.m. of nickel with each pass through the demetallization system. It is advisable, therefore, to operate the cracking and demetallization procedures with a catalyst having a metal content near the limit of tolerance of the cracker for poisoning metals. This, in turn, means that it is desirable to limit the total nickel 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 200 p.p.m. vanadium so that 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. Advantages of the 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. The actual time or extent of treating depends on various factors, and is controlled 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 amount 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 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 satisfactory treating rate may be about 5 to 10% 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. Copending patent applications Serial Nos. 758,681, filed September 3, 1958; 765,833 and 765,834, filed September 29, 1958; 767,794, filed October 17, 1958; 842,648, filed September 28, 1959; 849,199, filed October 28, 1959; 19,313, filed April 1, 1960; 39,810, filed June 30, 1960; 47,598, filed August 4, 1960; 53,380, filed September 1, 1960; 53,623, filed September 2, 1960; 54,368; 54,405 and 54,532, filed September 7, 1960; 55,129; 55,160 and 55,184, filed September 14, 1960; 55,703, filed September 14, 1960; 67,518, filed November 7, 1960; 73,199, filed December 2, 1960; and 81,256 and 81,257, filed January 9, 1961; all of which are hereby incorporated by reference, describe procedures by which vanadium and other poisoning metals included in a solid oxide hydrogen carbon conversion catalyst are removed by dissolving them from the catalyst or subjecting the catalyst, outside the hydrogen 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 regenered 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, and is preferably performed at a temperature at least about 50° F. higher than the regeneration temperature. Lower, 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° F, or even as high as 1600° F. The duration of the demetallization 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 content is 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 the typical size of passage through 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 crudes. Such treatment may be a basic aqueous wash such as described in copending patent applications Serial No. 767,794, and Serial No. 39,810. Alternatively vanadium may be removed by a chlorination procedure as described in copending application Serial No. 849,199.

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⁺, NH₃, NH₂⁻, or NH₃⁺ with one or more of the following: 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 3 hours or longer. After the ammonium wash the catalyst slurry can be filtered to give a cake which may be resulphured 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 moderately elevated temperature up to about 1000° F. is of value in removing vanadium contaminants from the catalyst as valuable chlorine compound. The treatment is described in co-pending application Serial No. 849,199. The chlorination takes place at a temperature of at least about 300° F,
preferably about 550 to 630° 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 regent.

The preferred activating 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 for example in combination of, for example, vapor phase 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 mix uniformly with the catalyst matrix. The chlorinating agent 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, and containing one percent or more SCl2 gives good results. Preferably, such a gas provides 1-10 percent Cl2 and about 1.5 percent SCl2 based on the catalyst. 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 disposing 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 in conjunction with the application Serial No. 763,834 and Serial No. 758,681, and may be accomplished by contacting the catalyst with a sulfating gas, that is SO2, SO3 or a mixture of SO2 and O2 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 the application Serial No. 763,834 and Serial No. 842,618, 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 H2S, CS2 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 1300° F, preferably about 800 to 1300° F. Other treating conditions include using 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 is generally based 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 sulfiding step. The sulfiding step is not a 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.

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, 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 O2 and at very brief contact times.

The metal sulfides may be rendered water-dispersible by a liquid aqueous oxidizing agent such as a dilute hydroxyl peroxide or hypochlorous acid water solution, as described in the pending application Serial No. 842,618. 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 50 pounds acid (on a 100% basis) to about 1 to 25 pounds or more H2O2 (also on a 100% basis) in a very dilute aqueous solution, to about one ton of catalyst. A 30% H2O2 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 or oxygen and maintaining 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, but the slurry form of the catalyst is more easily formed than the slurry form of the catalyst in a gaseous medium.
ter solutions of managanates and permanganaotes, chlorites, chlorates and perchlorates, bromites, bromates and per- bromates, lodates and periodates, are also useful. Bromine or iodine water, when oxidized; oxalated or mal- oxalated water, with or without acid, also will provide a dispersed form. The conditions of oxidation can be se- lected 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 provision of nickel sulfide in a dispersed form, the catalyst is washed with an aqueous medium to re- move the metal poisons. This aqueous medium, for best removal of nickel is generally somewhat acid. 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 atmos- pheric 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 oxidizing agent in order to avoid the undue solution of alumina from a chlorinated catalyst, contact time in this stage is preferably held to about 3 to 5 minutes which is suf- ficient for nickel removal. Also, since a slightly acidic solution is desirable for nickel removal, this wash pref- erably 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 re- moved 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. 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 atmos- pheric or less up to about 1000 p.s.i.g. with a vapor con- taining 10 to 100% hydrogen. Preferred conditions are a pressure up to about 15 p.s.i.g. and a temperature of about 800 to 1300° F. CO treatment serves generally both to convert the elemental metals, especially nickel to volatile carbonyl and to remove the carbonyl.

After the ammonium wash, or after the final treat- ment 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 in- ventory is demetallized, the catalyst may be returned to the cracking system, preferably to the regenerator stand- pipe, as a slurry in its final aqueous treating medium. Where a large amount of catalyst inventory is treated, the water put out the fire or unduly lower the tem- perature in the regenerator, it may be desirable first to dry a 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 above about 1100° F. may sometimes be disadvantageous. Calcination removes free water, if any is present, and per- haps 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 may then 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 conjunc- tion 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 com- pared with that which would have been removed if the particular step had not been performed. After the available catalytically active poisoning metal has been re- moved, in any removal procedure, further procedures may have relatively little effect on the catalytic activity of the deposited catalyst, although further metals con- tent may be removed by repeated or other treatments.

This invention will be better understood by reference to the accompanying drawings which shows the schematic of a representative processing system but is not to be construed as limiting.

A residual feed contaminated with poisoning metals, for example, a vacuum asphalt, is fed by line 10 to hydratation unit 12. The structure of the unit will, of course, depend upon the hydrogenation procedure; for instance in the HDDD method, the unit 12 may consist of a coil or a coil and drum. In this method the feed is heated in the coil to about 700 to 1200° F. and then contacted in the drum with a donor diluent, such as tetralin. The extent of conversion and the amount of metals removed will, of course, depend upon the severity of the hydrogenation and the characteristics of the original feed. In the alternative hydrogenation procedures, hydrogenation may be conducted under other conditions previously described. The hydrogen donor enters hydrotreater unit 18 by line 20. Line 20, along with the introduction of free hydrogen, if any is employed, suitable pumps, not shown, may be provided to mix the residual feed with the hydrogen donor. The con- ditions in the unit, 18, are adjusted for the results required. The total products are passed from the unit 12 to fra- ctionator 16 by line 18. Fixed gases are removed by line 20 and gasoline and lighter components having an end boiling point of about 430° F. are removed by line 22 to storage or further treatment such as hydroforming. The hydrogen donor diluent may be removed from the fractionator by line 24 and hydrogenated by means, not shown, before being reintroduced into the system by line 14 with fresh hydrogen donor diluent, if needed, from line 25. Gas oils having a boiling point within the range of about 400 to 700 or 800° F. may be re- moved by line 26 and carried directly to the catalytic cracker 28 by line 30 and 32 or it may be removed from fractionator 16 along with the bottoms fraction, which usually has a boiling point essentially above about 700 or 800° F. by line 34 and conducted to vacuum tower 36, where the combined gas oil and bottoms frac- tion-or the bottoms fraction, itself—are distilled at temperatures of about 750° F. and pressures of about 25 mm. Hg. Steam may be introduced by line 38. The residue, containing essentially heavier asphaltic constit- uents boiling above about 1050 or 1100° F., is removed from the vacuum tower by line 40 and may be con- ducted back to the hydrotreater by lines 40 and 10 for
further processing or may be withdrawn from the system by line 41. Vacuum gas oil containing cracking components of reduced metal content, is removed from the vacuum tower by line 42 and conveyed to the cracking by line 32. The cracking feed may be further diluted with low metals content conventional cracking stock from an outside source by lines 44 and 46. The cracker effluent leaves by line 50 and is brought to fractionator 52, where components of the effluent are withdrawn by line 54 for fixed gases, line 56 for gasoline, line 58 for components and line 59 for materials higher boiling than gas oil. The latter components may be withdrawn from the system by line 62 or may be recycled by lines 64, 66, 68 and 10 to the hydrogenation zone 12, for further processing. The gas oil fraction is preferably recycled to the catalytic cracking step by lines 58, 67, 48, 46 and 32 since it is substantially poison-free, or it may be withdrawn for use as distillate fuel by line 68.

Contaminated catalyst is continuously removed from the cracker by line 69 which conducts it to the regenerator 70. The regenerator is provided with the exit 72 for exhaust gases and with line 74 for the removal of regenerated catalyst and return to the cracker 28. A small slip stream of catalyst may be removed from line 74 for demetallization by line 76 and conveyed to demetallization unit 78. The demetallization unit 78 may comprise a system which includes apparatus (not shown), for example, for sulfiding, chlorineizing, washing and filtering the catalyst. Alternatively, instead of chlorinating the sulfided catalyst, means for oxidizing the sulfided catalyst may be substituted. The demetallization procedure used will, of course, depend upon the metals present. When, for instance, the feed to be treated contains predominant amounts of vanadium, the demetallization treatment will be geared mainly toward the removal of vanadium such as, for example, demetallization apparatus for high temperature treatment with molecular oxygen containing gas as disclosed in S.N. 19,313 followed by a basic wash as disclosed in application S.N. 39,810. After a substantial portion of the metal contaminants are removed from the cracking catalyst, the catalyst is returned to the cracking system by line 80.

The treating process of the present invention may be exemplified by the following:

A North Texas reduced crude having an API gravity of about 22°, a carbon content of about 5.3 weight percent, having an initial boiling point above about 650° F., and containing about 2.5 p.p.m. nickel and 60 p.p.m. of vanadium is mixed with a hydrogen donor diluent comprising a hydrogenated catalytic cycle oil in a 1 to 1 donor diluent-to-oil ratio and thermally cracked. The thermal cracking is operated at a temperature of about 800 to 900° F. and under a pressure of about 100 p.s.i.g. The feed rate is controlled so that the blend of reduced crude and donor diluent is held for about 30 minutes at about 820° F. About 40% of the 1050° F. + components of the crude are converted to gas oil and lower boiling products. The total products are conducted to a fractionator where C5 gases and gasoline having an end boiling point of about 430° F. are taken off at atmospheric pressure. The combined gas oil and bottoms fraction having a metals content of about 12 p.p.m. nickel and 20 p.p.m. vanadium is distilled at a temperature of about 750° F. and a pressure of about 25 m.m. Hg. The residue, containing material not suitable for catalytic cracking, is conveyed to the hydrogenation zone for further processing. The overhead fraction, amounting to about 85% of the feed to the vacuum still, containing materials boiling above 400° F. and containing 2 p.p.m. nickel and 6 p.p.m. vanadium is diluted with a recycle gas oil from the cracker fractionator. The feed to the cracking unit contains about 1.5 p.p.m. NiO and 4.5 p.p.m. V2O5. The catalytic cracker the feed contacts a synthetic gel silica-alumina catalyst, having an Al2O3 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 65% yield of gasoline and other components are removed. The gas oil fraction is recycled to the cracker. 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 0.4%.

About 5% per day of the cracking catalyst inventory poisoned to a metals level of about 280 p.p.m. NiO and 1025 p.p.m. vanadium is 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 H2S gas at a temperature of about

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The catalyst is then purged with flue gas at a temperature of about 575°F. for about 1 hour. The catalyst is quickly washed with water. A pH of about 2 is imparted to this wash medium by chloride entrapped 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.

A third run is conducted with a West Texas asphalt having an initial boiling point of about 950°F., a specific gravity of 1.002, a Conradson carbon content of about 20.3 and a metals level of 76 p.p.m. nickel oxide and 110 p.p.m. vanadium oxide. The feed is diluted with a substantially metals-free cycle oil in a ratio of 1 to 1 and sent to a hetrotreating operation as a mixture of liquid and vapor. The hydrotreater contains a fixed bed of cobalt-nickel-alumina catalyst analyzing about 2.5% Co and 9% MoO₃. In this 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 feed, about 250 s.c.f. of which are consumed. Condition C is a minimum and only about 5% of the asphalt feed is converted to products boiling below about 950°F. Hydrogen consumption is about 437 s.c.f./bbl. of feed. The hydrogenated product, analyzing about 5.5 p.p.m. nickel oxide and 10.2 p.p.m. vanadium oxide, is vacuum distilled at a temperature of 750°F. and a pressure of 25 mm. Hg. and the resulting gas oil boiling between 400 to 1100°F. and amounting about 35% of the hydrogenated product, analyzes 1.5 p.p.m. nickel oxide and 3.0 p.p.m. vanadium oxide. The vacuum gas oil is catalytically cracked at a temperature of about 950°F., at 10 p.s.i.g. pressure in the presence of a synthetic-gel silica-alumina catalyst containing about 13% Al₂O₃. The cracked products are introduced to a fractionator where a 60% yield of gasoline and other low boiling components are removed. The products boiling above about 950°F. are recycled to the hydrogenator for further processing. A portion of the silica-alumina catalyst is continuously removed from the cracking reactor and brought to a regenerator. A 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 0.5%. About 10% of the cracking catalyst inventory, poisoned to the extent of about 225 p.p.m. nickel and 910 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. then in H₂S for about an hour at 1150°F., and in a C₁₀/C₅₀ vapor mixture at 600°F. and then sent to a basic wash with an ammonium hydroxide solution having a pH of about 8 to 11. The catalyst 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 90 p.p.m. nickel and 665 p.p.m. vanadium.

This invention provides for overcoming poisoning effects by a balanced process which includes hydrogenation, distillation and cracking catalyst demetallization. It is claimed:

1. A process for treating a residual hydrocarbon oil boiling above the gasoline range and containing at least about 5 p.p.m. of a metal contaminant selected from the group consisting of nickel and vanadium in an amount sufficient to cause deterioration in selectivity of a cracking catalyst, comprising the steps of treating said hydrocarbon oil in a hydrogenation zone to reduce by about 10-50% the content of said contaminant metal, subjecting a thus hydrogenated fraction boiling essentially above about 400°F. to vacuum distillation to separate a gas oil fraction containing a metal contaminant selected from the group consisting of about 1-5 p.p.m. nickel and about 1-10 p.p.m. vanadium, said nickel and vanadium being calculated as the metal oxides, and an undistilled residue boiling primarily above about 1100°F. and containing asphaltic material, subjecting to catalytic cracking a hydrocarbon feedstock containing said gas oil fraction in an amount of at least about 0.5 p.p.m. of said contaminating metal, in the presence of a solid cracking catalyst under cracking conditions to produce gasoline, removing metal contaminated catalyst from the cracking system, the removed catalyst containing at least about 50 p.p.m. of a metal contaminant selected from the group consisting of nickel and vanadium, demetallizing said catalyst to withdraw about 10 to 90% of said metal contaminant, returning resulting demetallized catalyst to said cracking system and recovering the products from said cracking.

2. The process of claim 1 wherein the hydrogenation is carried out by mixing the residual hydrocarbon oil with a hydrogen donor diluent in proportions of about 0.1 to 10 volumes of diluent per volume of residual hydrocarbon oil, subjecting the mixture to temperatures in the range of about 700-1200°F. and pressures from about 1000 to 1500 psig. to a hydrogenated effluent fraction boiling primarily above about 950°F. is subjected to vacuum distillation.

3. The process of claim 2 wherein the hydrogenation is performed in the presence of about 1 to 10% of a hydride of a halogen having an atomic number of 35 to 53.

4. The process of claim 3 wherein the halogen hydride is hydrogen iodide.

5. The process of claim 3 wherein the halogen hydride is hydrogen bromide.

6. The process of claim 1 wherein the hydrogenation is carried out by contacting the residual hydrocarbon oil with hydrogen at temperatures of about 600 to 900°F. and pressures of about 300 to 3000 psig. with molecular hydrogen and a hydrogenation catalyst.

7. The process of claim 6 wherein the hydrogenation catalyst is a solid oxide of a hydrogenation promoting metal on a solid carrier.

8. The process of claim 1 wherein cracking catalyst demetallization includes contact of the catalyst with a vapor reactive with a metal contaminant.

9. The process of claim 1 wherein the solid cracking catalyst is a synthetic gel silica-based cracking catalyst.

10. A process for preparing gasoline from a residual hydrocarbon oil boiling above the gasoline range and containing a metal contaminant selected from the group consisting of nickel and vanadium which comprises contacting a cracking feedstock containing at least about 0.5 part per million of said metal contaminant with a solid synthetic gel silica cracking catalyst under cracking conditions to produce gasolines, removing the cracking system catalyst contaminated with said selected contaminant, demetallizing the catalyst, retaining catalyst to said cracking system, and recovering gasoline product from said cracking; said feedstock containing the vacuum gas oil fraction obtained by treating the residual hydrocarbon oil boiling above the gasoline range and containing metal contaminant in a hydrogenation zone to reduce partially the content of said contaminant metal by at least about 10% and subjecting a hydrogenated fraction boiling essentially above about 400°F. to vacuum distillation at a temperature of about 700-775°F. and a pressure of about 10-30 mm. Hg.:

11. The method of claim 9 wherein the catalyst is silica aluminia.

12. A process for treating a residual hydrocarbon oil boiling above the gasoline range and containing about 10 to 500 p.p.m. nickel and about 10 to 1000 p.p.m. vanadium and in an amount sufficient to cause deterioration in selectivity of a synthetic gel silica-based cracking catalyst, comprising the steps of treating said hydrocarbon oil
oil in a hydrogenation zone to reduce by about 50 to 90% the content of said contaminant metals, subjecting a thus hydrogenated fraction boiling essentially above about 400°F, to vacuum distillation to separate a gas oil fraction containing about 1-6 p.p.m. nickel and about 1-10 p.p.m. vanadium, said nickel and vanadium being calculated as the metal oxides, and an undistilled residue boiling primarily above about 1100°F, and containing asphaltic material, subjecting to catalytic cracking a hydrocarbon feedstock containing said gas oil fraction in an amount to provide about 0.5 to less than about 4 p.p.m. nickel and about 0.5 to less than about 5 p.p.m. vanadium, in the presence of a solid, synthetic gel, silica based cracking catalyst under cracking conditions to produce gasoline, removing metal contaminated catalyst from the cracking system, the removed catalyst containing at least about 200 p.p.m. of nickel and at least about 500 p.p.m. vanadium, demetallizing removed catalyst to withdraw at least 50% of the nickel and at least 15% of the vanadium, returning resulting demetallized catalyst to said cracking system and recovering the products from said cracking.

13. The method of claim 12 wherein the catalyst is silica-alumina.

14. The method of claim 13 in which catalyst from the catalytic cracking is regenerated to remove carbon and demetallized by contact with an oxygen-containing gas at a temperature of about 1000 to 1800°F, to enhance subsequent vanadium removal, sulfided by contact with a sulfiding agent at a temperature of about 500 to 1500°F, to enhance subsequent nickel removal, 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, and contacting the catalyst with a liquid, essentially aqueous medium to remove soluble poisoning metal components from the catalyst.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,162,596

December 22, 1964

Arvin D. Anderson et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 13, line 68, for "application" read -- applications --; column 16, line 31, for "drawings" read -- drawing --; column 20, line 16, for "resulting" read -- resulting --; line 47, for "catalyst" read -- catalyst --; column 21, line 5, for "1-6" read -- 1-5 --.

Signed and sealed this 29th day of June 1965.

(SEAL)

Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents