Jan. 20, 1959 F. E. FREY 2,870,081

REMOVAL OF METAL CONTAMINANTS FROM HYDROCARBON LIQUIDS AND IMPROVED HYDROCARBON CONVERSION PROCESS

Filed April 11, 1955 3 Sheets-Sheet 1

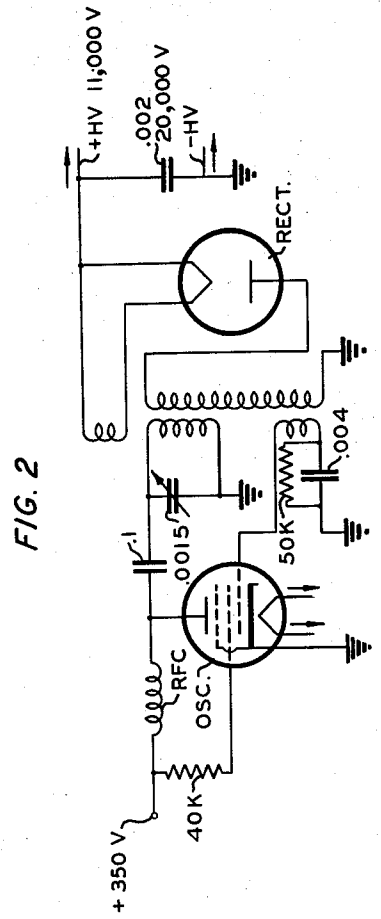


FIG. 2

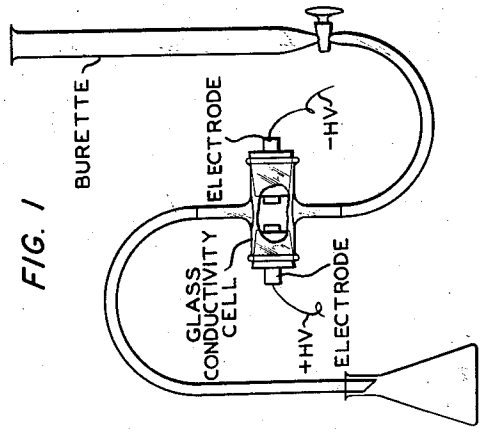


FIG. 1

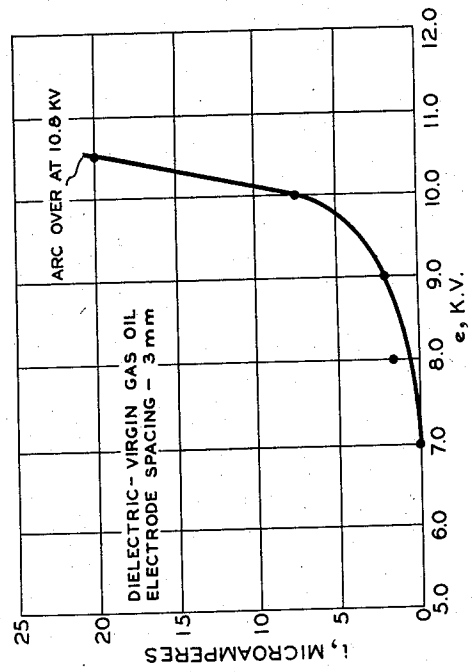


FIG. 3

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FIG. 4

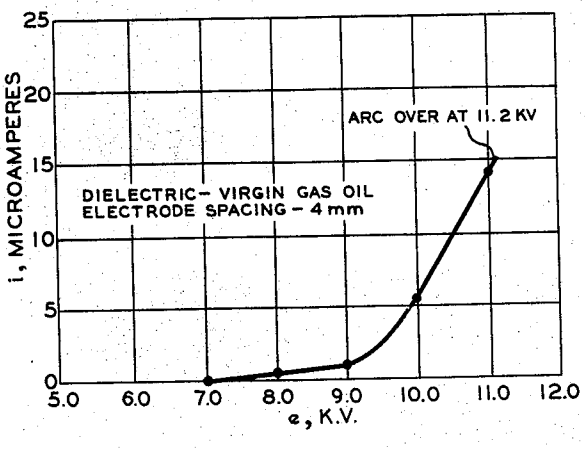


FIG. 5

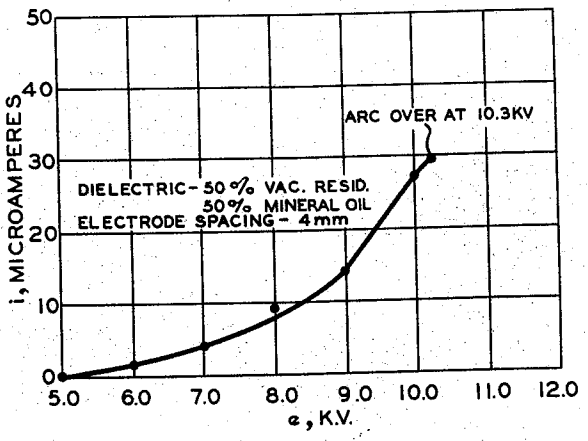
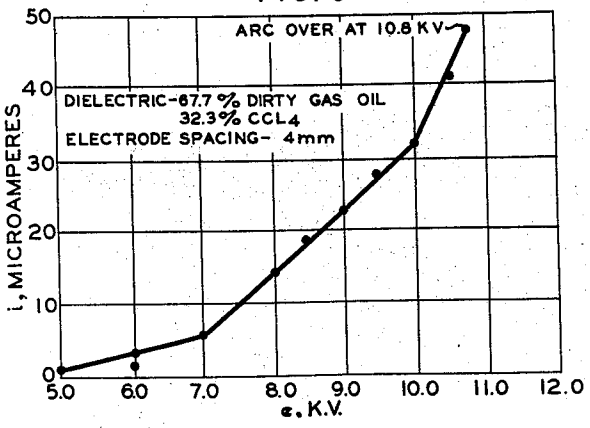


FIG. 6



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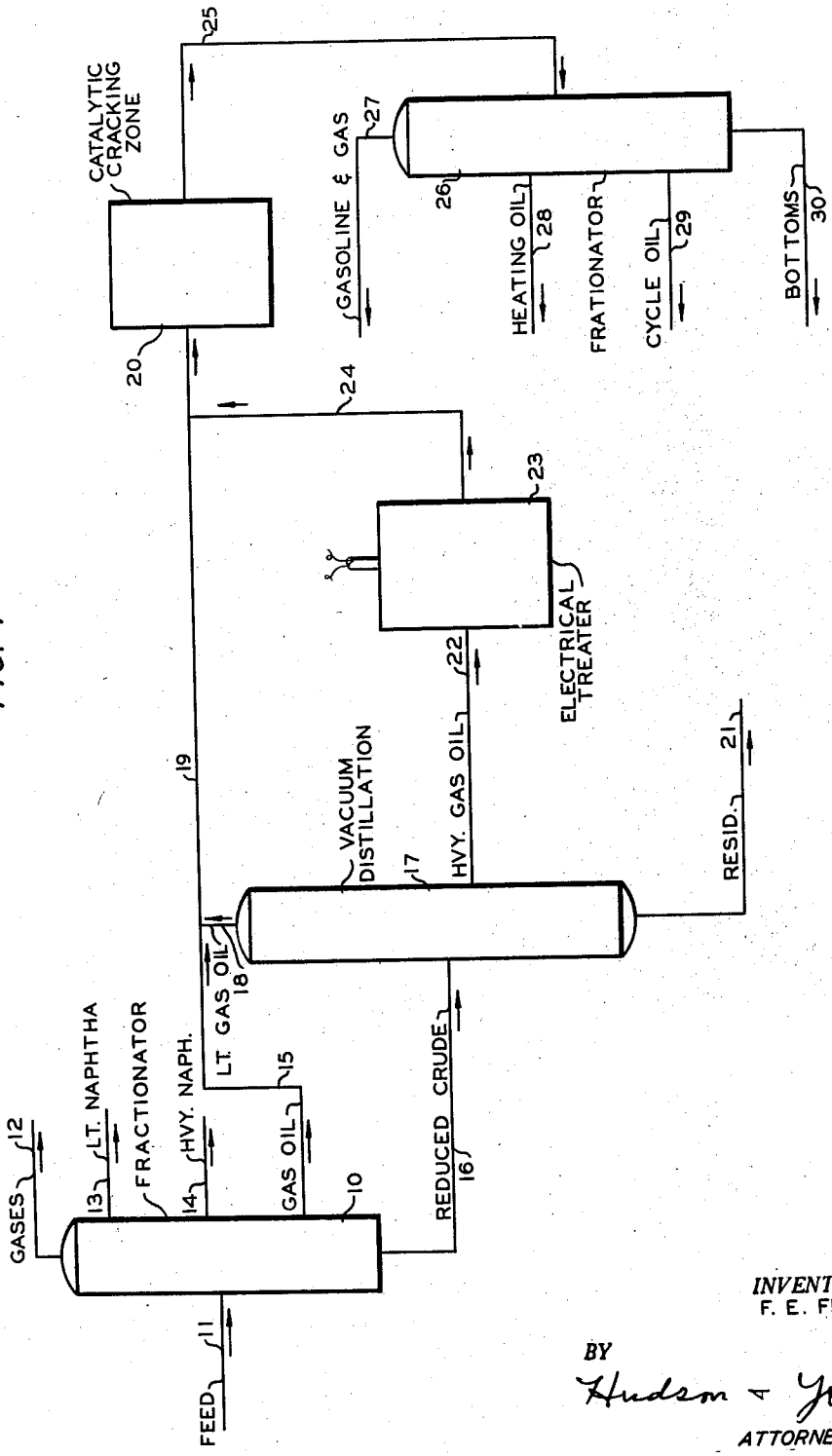
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FIG. 7



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REMOVAL OF METAL CONTAMINANTS FROM HYDROCARBON LIQUIDS AND IMPROVED HYDROCARBON CONVERSION PROCESS

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Application April 11, 1955, Serial No. 500,469

10 Claims. (Cl. 208—88)

This invention relates to the removal of metal contaminants from hydrocarbon liquids. In one of its aspects, the invention relates to the removal of metals or metal-containing compounds from a hydrocarbon oil by subjecting said oil to a high tension electrical field. In another of its aspects, the invention relates to the preparation of a catalytic cracking feed stock from an oil containing metal-containing contaminants such as prophyrins. In still another of its aspects, the invention relates to the concentration of the said contaminants, as they are found in a feed stock, into a selected fraction which is then subjected to said electrical field, thus reducing the size of equipment required to remove said contaminants from the oil. In a further aspect of the invention, there is provided a combination of steps in a unitary process which includes distilling a metal contaminated feed stock to obtain therefrom a gas oil and a reduced crude bottoms, said reduced crude bottoms containing heavy gas oil and residual oil; vacuum distilling said reduced crude bottoms to obtain therefrom as overhead a light gas oil, which is combined with said gas oil earlier obtained, a heavy gas oil, and a residue; subjecting said heavy gas oil to a high tension electrical field so as to remove therefrom substantially all metal contaminants which have been concentrated therein; combining the thus-treated heavy gas oil with the earlier mentioned and combined gas oils and subjecting said total gas oils to a catalytic cracking operation and recovering a catalytically cracked product stream.

Other aspects, objects, as well as advantages of the invention are apparent from a study of this disclosure, the drawings, and the appended claims.

The catalytic cracking process has become increasingly important to the petroleum industry as the competitive demand for higher octane motor fuel has developed. The function of the catalytic cracking process is to convert a hydrocarbon fraction known as gas oil into gasoline-fuel oil, gas and coke being produced as by-products. Relative yields of gasoline and by-product fuels or oils may be influenced by the quality of the catalyst. The term "catalyst selectivity" denotes the inherent catalytic properties that control these relative yields. Catalyst selectivity is usually expressed in terms of hydrogen and coke production, and a catalyst of good selectivity produces relatively lower yields of both hydrogen and coke.

Investigations in the field of catalytic properties have shown that deterioration of catalyst selectivity with time can be caused by the presence of relatively small quantities of contaminants in the feed. Known catalyst "poisons" that adversely affect selectivity are sulfur and metals. Iron, nickel, vanadium, and copper are the major metallic contaminants commonly found in gas oil feeds. The metallic compounds are relatively nonvolatile and are found in greatest concentrations in the higher boiling crude fractions and may be carried by entrainment to the catalyst wherein they accumulate. Both natural and synthetic catalysts are poisoned in this way.

To increase the production of catalytic gasoline, the refiner usually wishes to augment the catalytic cracking

feed with contaminated marginal streams, or even with whole crude. However, the resulting decline in catalyst selectivity makes such a procedure disadvantageous in the long run. Although it is possible for the refiner to control the selectivity deterioration by continually discarding a fraction of the catalyst in the unit and replacing it with fresh material of good selectivity, this expedient increases operating costs because of its additional catalyst consumption.

Essentially no metals are found in most petroleum distillates which boil below 800 F. at one atmosphere pressure. However, there is available in most crudes, in the boiling range of 800 to 1200 F. or higher, a considerable amount of oil which would be a good cracking stock if it could be recovered sufficiently free of metals, preferably having less than 1 part per million of nickel oxide or vanadium oxide content. Since it is generally assumed that vacuum distillation and flashing are by far the cheapest means of recovering these heavy gas oils, this method is generally employed. As one goes deeper into the crude, in recovering these gas oils, there is obtained an appreciable amount of metal contamination either by volatilization or by entrainment, or both.

I have found that naturally occurring metal contaminants, especially nickel and/or vanadium, present in petroleum hydrocarbon oils can be effectively removed from the oil by subjecting the metals-contaminated hydrocarbon oil to a high potential direct current electrical field.

Therefore, according to this invention, there is provided a process for the removal of metal contaminants from hydrocarbon oils which comprises subjecting the said contaminated hydrocarbon oils to a high potential direct current electrical field.

Also, according to the invention, there is provided in an embodiment thereof, a process for the obtaining of valuable products from virgin petroleum hydrocarbon oils which are contaminated with metal-containing materials which process comprises the steps of (1) subjecting a metals-contaminated virgin topped crude to vacuum distillation or to flashing to obtain a heavy vacuum gas oil containing fraction, (2) subjecting said heavy gas oil-containing fraction to a high potential electrical field, and (3) subjecting the metals-free heavy gas oil fraction thus obtained to a fluid or other catalytic cracking operation to convert said gas oil to gasoline.

Still further, according to the invention, there is provided a process for the removal of metal-containing contaminants from oils which comprises subjecting the said oils to a high potential electrical field, preferably after removing lower boiling constituents from said oils to obtain a heavy gas oil type fraction.

The minimum field intensity utilized in the practice of this invention will vary somewhat depending on the particular oil charged to the process. In general it will be in excess of 15,000 volts per centimeter, but, in some instances, it may be below this value. The general range is approximately 15,000–30,000 volts per centimeter. It is preferred to operate at field intensities sufficiently high as to ensure that operation is in the Wien region of maximum ion velocities, which is just below the arc-over potential. By the application of very high voltages the ion may be forced to move fast enough to escape completely from its ionic atmosphere, so that the retarding forces disappear and the equivalent conductance approaches its limiting value at infinite dilution. The field intensities required will vary with the oil charged as shown by Figures 3, 4, 5, and 6, but in any given instance the required field intensity may be determined by routine test. These tests may be carried out by simply measuring the conductance of the oil at a series of voltages up to approximately the arc-over potential. When the current values are plotted against

the respective voltages, as shown in Figures 3 to 6, the initial and final portions of the resulting urve will be approximately linear. The final linear portion of the curve represents the Wien region of maximum ion velocities.

Although the mechanism taking place in the present invention is not fully understood, the removal of deleterious metallic components from petroleum stocks may, possibly, be accomplished as a result of ionization and migration of polar metal bearing molecules, induced polarization and migration, or by the opening of ring structures which contain tightly bound metallic atoms.

In carrying out this process the heavy vacuum gas oil may be pumped at normal temperatures if it is sufficiently fluid or at elevated temperatures sufficiently high to obtain mobility and fluidity, into the electrical treater without previous dilution to reduce viscosity, and subjected to a high potential electrical field as previously described. However, in case the viscosity of the oil is too high for practical purposes it can be cut back to reduce the viscosity. The viscosity reducing material is preferably a lighter petroleum fraction and, in any event, should be nonpolar.

In Figure 1 there is shown a glass-conductivity cell in which certain oils were processed as indicated in the examples. Figure 2 shows an R. F. excited power supply. Figures 3, 4, 5, and 6 show voltage-current relationships for the oils tested showing that the cell could be operated in the Wien region of maximum ion velocities. Figure 7 shows a diagrammatic flow plan of a specific embodiment of the invention which is later described.

The process of the present invention may be readily understood by reference to Figure 7 which illustrates a specific embodiment of the same.

Referring specifically to Figure 7, a feed oil, for example, a West Kansas or West Texas crude, is introduced into fractionator zone **10** by means of feed line **11**. Temperature and pressure conditions in zone **10** are adjusted to secure the desired fractionation of the crude oil so as to obtain products now mentioned. The operating conditions in the distillations and in the cracking steps are readily selected depending upon the exact nature of the feed and of the product fractions desired. Low boiling hydrocarbon gases are removed overhead from zone **10** by means of line **12**; a hydrocarbon fraction boiling in the light naphtha range is removed by line **13**, a hydrocarbon fraction boiling in the heavy naphtha range by line **14**, while a gas oil fraction is removed by line **15**. A fraction boiling in the reduced crude boiling range, for example, in the range above about 600 to 700° F., preferably boiling in the range above 750° F., is segregated as a bottoms fraction by means of line **16**. Zone **10** may comprise any suitable number and arrangement of fractionation zones or stages. The high boiling reduced crude is passed, by line **16**, to vacuum distillation zone **17**. Temperature and pressure conditions in zone **17** are adjusted to secure the desired vacuum distillation of the reduced crude. Thus, the temperature in the tower bottoms will usually be in the range 700–800° F. and the pressure will be usually in the range of 1–300 mm. Hg. A light gas oil fraction is removed from zone **17** by line **18**, and combined with the gas oil fraction removed from zone **10** by line **15**, and both passed through line **19** to catalytic cracking zone **20**. A residual fraction is removed from zone **17** by line **21**. A heavy gas oil fraction, which is the metals contaminated oil, is removed from zone **17** by line **22** and passed to electrical treater **23**, wherein the oil is subjected to a high potential electrical field, to substantially reduce the metals content of the oil. The action of the electric field on the metals-containing heavy gas oil passing between the electrodes is such that the metals are deposited on the surfaces of the electrodes. The high voltage direct current potential in the electrical treater is applied to the electrodes through suitable electrical connections from a source of high voltage direct current such as, for example, supplied by an A. C. generator, a step-up transformer, and a mechanical rectifier. The metals deposited on the electrodes may be either removed continuously or intermittently by any suitable means. The electrically treated heavy vacuum gas oil, which is substantially free of undesirable iron, vanadium, and nickel and other compounds, is removed from electrical treater **23** by line **24** and introduced into a fluid catalytic cracking operation along with the gas oils present in line **19**. The fluid catalytic cracking plant **20** is composed of three sections: cracking, regeneration and fractionation. Temperature and pressure conditions in cracking zone **20** are adjusted to secure the desired conversion of the feed oil and are conventional. Cracked products are removed from zone **20** by line **25** and passed into fractionator zone **26**. Hydrocarbon constituents boiling in the gasoline and lower boiling ranges is removed overhead from zone **26** by line **27**. A heating oil fraction is removed by line **28** while a fraction boiling in the light cycle oil boiling range is removed by line **29**. A bottoms fraction or heavy cycle oil is removed by line **30** and handled as desired. A plurality of treaters such as **23** can be used simultaneously or in rotation and from time to time can be cleaned by flushing or otherwise as desired.

Thus by the practice of the present invention, residual stocks which would otherwise have to be sold as low cost, heavy fuel oil or otherwise used as low grade, heavy products are converted to valuable catalytic cracking feed which may be cracked over catalysts, without undue contamination, to yield high octane gasoline and other valuable products normal to the fluid catalytic cracking operation.

The boiling ranges of the process streams described in Figure 7 can vary considerably; however, exemplary boiling ranges of some of the process streams follow: The charge oil passed to zone **10** can be a full range crude such as, for example, a West Texas or West Kansas crude. The gas oil withdrawn from zone **10** through line **15** boils between about 400–600° F. The reduced crude removed from zone **10** and passed to the vacuum unit boils above about 600° F. The light gas oil product removed from the vacuum unit boils between about 600–700° F., while the heavier metals contaminated gas oil passed to the electrical treater boils between about 700–1100° F., whereas the vacuum residium boils above about 1100° F. The combined gas oils passed as feed to the catalytic cracking unit boil between about 400–700° F.

EXAMPLE

To illustrate the operation of the present invention, gas oils and cut back heavy oils are subjected to electrical fields of 25,000 to 30,000 volts per centimeter to improve the quality of the oils by reducing the metal content. The equipment used consisted of a simple glass conductivity cell employing spectrographic quality electrodes as shown in Figure 1, and a high voltage R. F. excited direct current power supply as shown in Figure 2, and instruments to measure the field intensity. Conductivities of the various oils mentioned above were investigated by increasing the voltage up to approximately the arc-over potential and observing the current flow through the oil. Such voltage-current relationship for the oils tested are shown in Figures 3, 4, 5 and 6. The initial and final portions of the resulting curve was approximately linear. The final linear portion of the curve represents the Wein region of maximum ion velocities.

A vacuum unit dirty gas oil high in metals content cut back with 32 percent of CCl_4 was treated in the high voltage cell at a charge rate of 4.0 ml. per minute with an electrode spacing of 4.0 mm. and a field intensity of 26 kv. per centimeter. Colorimetric analysis for metals indicated reductions in metal content of 18.5 percent of nickel as NiO and 48.0 percent of vanadium as V_2O_5.

Colorimetric analysis of the untreated and treated gas oil is presented in the following table:

[Colorimetric metal analysis, p. p. m.]

	NiO	V_2O_5
Vacuum Unit dirty gas oil	24.5	95.1
High Voltage treated vacuum unit dirty gas oil	16.7	64.5

Reasonable variation and modification are possible within the foregoing disclosure, drawings and the appended claims to the invention, the essence of which is that metal contaminants which are present in oils are removed therefrom by submitting said oils to a high tension electrical field, as described, and that in one embodiment of the invention there has been provided a unitary process in which the contaminants are concentrated into a heavy gas oil fraction which is treated with such a field, and further, as described, there is provided a combination of steps which include a distillation of a feed, concentration of the metal contaminants in a heavy gas oil fraction, treating the heavy gas oil fraction with a high tension electrical field, as described, and then combining the said treated gas oil with other gas oil obtained in the distillation of the feed and submitting the combined gas oils to a catalytic cracking, also substantially as described.

I claim:

1. A process for the conversion of a virgin topped crude which comprises removing metal-containing contaminants from the oil during its treatment and before it is subjected to a cracking operation which comprises vacuum distilling said topped crude to recover as a product a heavy vacuum gas oil, subjecting the heavy gas oil to a high potential direct voltage electrical field in the approximate range of 15,000–30,000 volts per centimeter sufficient to reduce the metals content thereof and then subjecting the substantially metals-free heavy gas oil to a catalytic cracking operation under conditions adapted to crack said oil into useful products.

2. A process for removing metal-containing contaminants from an oil which comprises subjecting said oil to an electrical field of at least approximately 15,000 volts per centimeter for a time sufficient to remove from said oil said contaminants and then recovering said oil free from said contaminants.

3. A process for removing from an oil, metal-containing contaminants which are present therein as metal-porphyrin complexes, which comprises subjecting said oil to a direct voltage electrical field of at least approximately 15,000 volts per centimeter for a time sufficient to remove from said oil said contaminants and then recovering said oil free from said contaminants.

4. In the processing of a crude oil containing metal-porphyrin complex contaminants, the steps in combination which comprise distilling said crude oil; obtaining among the products of the distillation a gas oil and a reduced crude; passing said gas oil to a catalytic cracking zone; subjecting said reduced crude to a vacuum distillation to obtain a light gas oil, a heavy gas oil and a residue; feeling said light gas oil together with said first-mentioned gas oil to said catalytic cracking zone; subjecting said heavy gas oil to a direct voltage high potential electrical field of at least approximately 15,000 volts per centimeter for a time and in a manner so as to remove a substantial portion of the said contaminants therein therefrom; and then also feeding said heavy gas oil to said catalytic cracking while operating said catalytic cracking zone under conditions to obtain from the combined oil streams fed thereto useful products.

5. In a process for removing metal-containing contaminants of the metal-porphyrin complex type from a hydrocarbon oil containing the same, the step which comprises subjecting said oil to an electrical field of direct current of at least approximately 15,000 volts per centimeter for a time sufficient to remove from said oils said contaminants and then recovering said oil free from said contaminants, the oil when subjected to said electrical field having been heated to a temperature of at least that at which it will distill.

6. A process according to claim 5 wherein the electrical field potential is approximately 25,000–30,000 volts per centimeter.

7. In the processing of crude oil containing metal-porphyrin complex contaminants to remove the same wherein the oil is distilled and there is obtained among the products of the distillation a gas oil and a reduced crude, wherein the gas oil is passed to a catalytic cracking zone, wherein the reduced crude obtained is subjected to a vacuum distillation to obtain a light gas oil, a heavy gas oil and a residue, wherein said light gas oil together with said first-mentioned gas oil is fed to a catalytic cracking zone, and wherein said heavy gas oil is finally also fed to said catalytic cracking zone, the improvement which comprises subjecting said heavy gas oil to a high potential direct voltage electrical field so as to remove a substantial portion of the metal-porphyrin complex containing contaminants therefrom, said field being of the order of at least about 15,000 volts per centimeter.

8. In a process for the conversion of a virgin topped crude wherein metal-porphyrin containing contaminants are removed from the oil during its treatment and gas oils obtained are subjected to a cracking operation, wherein said topped crude is vacuum distilled to recover as a product a heavy vacuum gas oil and said heavy gas oil is treated to remove said contaminants, and wherein said heavy gas oil is finally subjected to catalytic cracking, the improvement which comprises subjecting said heavy gas oil to a high potential direct voltage electrical field of the order of at least about 15,000 volts per centimeter, sufficient to reduce the metals content thereof.

9. A process according to claim 8 wherein the potential of the electrical field is in the approximate range of 15,000–30,000 volts per centimeter.

10. A process according to claim 8 wherein the electrical field potential is in the approximate range of 25,000–30,000 volts per centimeter.

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