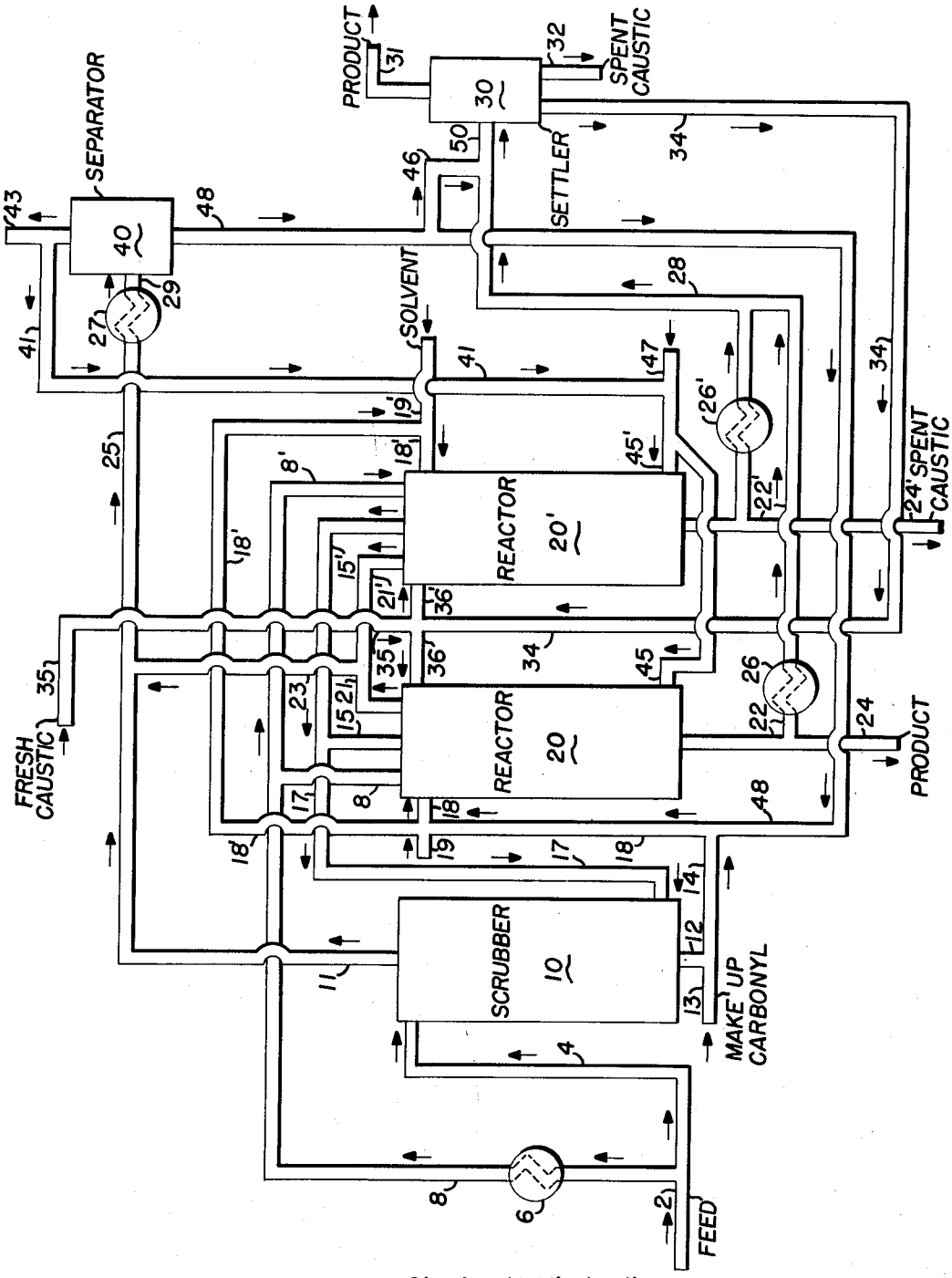
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DESULFURIZATION OF HYDROCARBONS WITH AN IRON GROUP CARBONYL IMPREGNATED ON AN ADSORBENT

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DESULFURIZATION OF HYDROCARBONS WITH AN IRON GROUP CARBONYL IMPREGNATED ON AN ADSORBENT

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The present invention is concerned with the desulfurization of sulfur-containing hydrocarbons. The invention more particularly relates to a method for desulfurizing a sulfur-containing petroleum fraction by contacting the fraction with a metal carbonyl under conditions of temperature, pressure and time and in the presence of a particulate solid having a large surface area such that the metal carbonyl decomposes to form the pure metal and carbon monoxide. The metal then combines with the sulfur in the petroleum fraction to provide the desired degree of desulfurization. The invention is especially effective for the desulfurization of high boiling petroleum reduced crudes and residua.

The problem of sulfur removal from petroleum fractions, crude oils and other mixtures of hydrocarbons is substantially as old as the petroleum industry itself. For most purposes, it is undesirable to have an appreciable amount of sulfur in any petroleum feed stock or product. The presence of the sulfur gives rise to serious corrosion and refining problems that are met and resolved only with considerable effort and expense.

The presence of sulfur in petroleum products is especially undesirable. Gasoline, for example, should be relatively free of sulphur in order to make it compatible with lead and to improve its color and odor stability. Furthermore, a decreased sulfur content in a gasoline automatically means an increased lead susceptibility for the gasoline. Sulfur is also objectionable in fuel oil of any kind because it burns to form sulfur compounds which are generally obnoxious and corrosive.

In an effort to combat the presence of sulfur in petroleum crude oils, feed stocks and products, the petroleum industry has resorted to a wide variety of desulfurization and sweetening processes. Furthermore, a large number of other processes is being suggested and developed as time progresses. For example, it has been suggested that sulfur-containing hydrocarbon mixtures be desulfurized by contacting the mixtures with an iron group metal carbonyl in the absence of hydrogen. It has been established that such a metal carbonyl decomposes under certain conditions of temperature and pressure to form the pure metal which in turn readily reacts with and removes sulfur from a hydrocarbon mixture.

Another procedures that has been suggested for desulfurizing a mixture of hydrocarbons consists in contacting the mixture with a finely divided particulate solid having a large surface area per unit weight such as activated char, silica gel, activated alumina, montmorillonite clay, bentonite and other natural clays. It has been found that such materials are moderately effective at temperatures of about 75 to 200° F. in reducing the sulfur content of the materials treated.

In accordance with the present invention, it has now been found that a markedly increased degree of desulfurization may be achieved by contacting a sulfur-containing hydrocarbon mixture with an iron group metal carbonyl in the presence of a particulate solid such as described above that possesses a large surface area per unit weight. In accordance with the invention, it has been specifically found that contacting a hydrocarbon mixture simultaneously with a metal carbonyl and a particulate solid affords a degree of desulfurization activities which is unusual and unexpected in comparison with the degrees of desulfurization that are attainable by either treating agent alone.

It is apparent from the foregoing statement that it is an object of the present invention to afford a new and different procedure for desulfurizing sulfur-containing hydrocarbon mixtures. It as a particular object of the invention to provide a procedure which is especially effective in desulfurizing petroleum fractions and especially petroleum fractions that boil above about 200° F. These and other objectives will be readily apparent from the description which follows.

In accordance with the present invention, a sulfur-containing mixture of hydrocarbons is contacted with an iron group metal carbonyl in the simultaneous presence of a particulate solid having a large surface area under conditions that are adapted ot decompose the metal carbonyl into carbon monoxide and finely divided metal. Under these same conditions the metal reacts with the sulfur in the hydrocarbon mixture to form insoluble products such as a sulfide of the metal. The desulfurized mixture is withdrawn from the treating zone generally in admixture with the carbon monoxide which has been formed by decomposition of the carbonyl. Having been withdrawn from the zone, the desulfurized mixture may then be separated from the carbon monoxide in a conventional manner as, for example, by a simple phase separation procedure.

Feed stocks that are adapted for processing in accordance with the present invention include hydrocarbons that boil above about 200° F. Feed stocks that are particularly well handled in accordance with the invention are petroleum fractions that boil above 450° F., such as gas oils, reduced crudes, and other residua. The invention is especially effective and attractive for the desulfurization of petroleum fractions of a residual type that boil above 750° F.

The feed stocks to the process of the invention may consist of cracked hydrocarbons as well as straight run hydrocarbons. The invention is best employed on feed stocks that are utilized in further refining operations or that are products from operations without previous desulfurization. These include naphtha feeds to hydroforming operations, gas oil feeds to catalytic cracking processes, residua stocks to coking operations, catalytic naphtha, coker naphtha and the various products from the coking of residua.

The amount of sulfur that the feed stock may contain has little or no critical effect on the functioning of the process. The process, however, is most effectively utilized with feed stocks that contain more than about 0.3 wt, percent sulfur and especially above 1.0 wt. percent sulfur. It will be observed that the greatest amount of sulfur that a feed stock would be contemplated to possess would be of the order of about 5 wt. percent. In this connection, it follows that the invention is especially well suited for the desulfurization of petroleum fractions such as naphthas and gas oils which conventionally contain from about 0.5 to 3 wt. percent sulfur.

As mentioned earlier, the process of the present invention requires the presence of a metal carbonyl in which the metal is an iron group metal; and for the purposes of the present description, metals of the iron group are considered to include iron, nickel and cobalt. It should be noted, however, that the carbonyls of these metals are not necessarily equivalent to one another in their

performance in the present process; and it has been found that nickel carbonyl is particularly preferred in carrying out the process.

The preparation, properties and chemical characteristics of the aforementioned metal carbonyls are well known in the art, and a lengthy discussion concerning these details is not considered to be a necessary feature of the present description. It will be briefly noted, however, that such carbonyls are conventionally formed by reacting the metals with carbon monoxide under selected conditions of temperature, pressure and time. It will also be noted that the carbonyls decompose very readily at certain other conditions of temperature and pressure to revert back to carbon monoxide and the pure metal. The pure metal as formed by the decomposition of the carbonyl has been observed to possess an extreme degree of chemical activity.

Particulate solids having a large surface area that are suitable for the purposes of the present invention are those materials that are conventionally employed in situations where large surface area supports are desirable or necessary. For example, it is conventional in the contacting of liquids, gases and similar fluids to employ finely divided solids in order to improve the degree of contact between the fluids. Such solids are also widely employed as supports in the manufacture of catalytic materials. Thus, it is conventional practice to impregnate particulate solids that have a large surface area with catalytic agents such as finely divided metals and the like. With this in mind, it is apparent that particulate solids that are suitable for use in the present invention are solids that are substantially non-reactive with hydrocarbons or iron group metal carbonyls. They may possess adsorbtive qualities and preferably possess surface areas of at least 100 square meters per gram and preferably at least 500 square meters per gram. It is well to note that many suitable materials may have surface areas as much as 1500 square meters per gram.

Particularly suitable solids for the purpose of the present invention include clays such as bentonite clays, montmorillonite clays and acid-treated natural clays; activated chars such as coconut charcoal, bone char, wood charcoal; and other conventional materials such as silica gel, activated alumina, magnesia, and the like.

Insofar as the particle size of the solids is concerned, it should be noted that this characteristic of the solids may vary depending upon the type of operation that is employed for carrying out the process of the invention. Thus, it is well known in the art and especially in the petroleum industry to use finely divided solids in the form of fixed beds, moving beds and so-called "fluidized beds." In fixed beds it is generally desirable that the solids possess a particle size within the range from about 3 to 15 millimeters and preferably of the order of about 10 millimeters. In moving beds the solids should have a particle size of about 0.5 to 10 mm. and preferably about 5 mesh. In fluidized beds it is generally necessary to have a particle size range of from about 0.01 to 0.5 mm. and preferably from about 0.02 to 0.10 mm. At this point, it will be noted that it is contemplated that the objectives of the invention are best realized by the use of fixed beds.

In setting out the conditions that are required for the successful operation of the present process, it will first be noted that the feed rate of the hydrocarbon material through the bed should be at least about 0.25 volume of feed expressed as liquid per volume of solids per hour. A feed rate within the range of about 0.5 to 2 v./hr./v. is particularly preferred; and it is contemplated that a feed rate of about 1 v./hr./v. is especially effective in most instances.

The feed to be desulfurized may be in the liquid and/or vapor phase and may be passed through the bed in either vertical direction. When the feed is primarily in the liquid phase, it is contemplated that the best manner of

operation is one wherein the feed is passed downwardly through the bed. Thus, this type of flow is generally preferred for the high boiling fractions which, as mentioned earlier, are particularly well processed in accordance with the invention.

The metal carbonyl may be introduced within the treating zone either separately or in conjunction with the hydrocarbon feed. Furthermore, when the carbonyl is separately injected into the treating zone, it may flow countercurrently with respect to the hydrocarbon stream. It is contemplated, however, that the best manner of operation is one wherein the carbonyl stream flows concurrently with respect to the hydrocarbon stream. It is further contemplated that the best manner of introducing the carbonyl within the treating zone is with the hydrocarbon stream.

The feed rate of the carbonyl stream should be such that at least about 1 mol. of metal per mol. of sulfur (in the hydrocarbon stream) is introduced within the treating zone. The amount of carbonyl must be sufficient to provide the desired degree of desulfurization with due regard to the other operating conditions that are employed. Thus, the amount of carbonyl is generally inversely related to the temperature of the treating zone and the treating time and directly related to carbon monoxide partial pressure. These considerations of temperature and carbon monoxide partial pressure are applicable to conditions wherein the decomposition of the nickel carbonyl is incomplete and the metal available for desulfurization is that permitted by the particular equilibrium condition. However, in most of the contemplated operations the temperature will be sufficiently high and the carbon monoxide partial pressure sufficiently low so as to permit essentially complete decomposition of the carbonyl and hence the desulfurization requirement of one mol. of metal per mol. of sulfur in the feed is approximately one mol. of metal carbonyl per mol. of sulfur in the feed. For satisfactory operation in most instances, the amount of carbonyl introduced within a treating zone should be such as to provide from about 1 to 2 mols of the metal per mol of sulfur that is introduced within the zone during the same time interval.

As mentioned above, the temperature within the treating zone must be at least sufficient in value to cause the metal carbonyl to decompose into carbon monoxide and the metal itself. In the case of nickel carbonyl, a temperature of the order of about 30 to 40° C. generally causes decomposition of this compound at low carbon monoxide partial pressures. With iron and cobalt carbonyl, the decomposition temperatures are somewhat higher. With this in mind, it is contemplated that the treating temperature should be within the range from about 500 to 800° F. and preferably about 700° F. The precise temperature to be employed is governed to some extent by other factors as, for example, the nature of the feed stock. In general, the treating temperature is directly related to the boiling point range of the hydrocarbon feed.

The pressure within the treating zone should be such that the vapor pressure requirements of the feed and reaction products be satisfied at any of the operating temperatures and with any of the desired feed stocks. Thus, an operating pressure of between 300 and 900 p. s. i. g. and especially about 500 p. s. i. g. is preferred.

As the treating reaction occurs and progresses, the hydrocarbon feed reacts with the decomposition products of the metal carbonyl to form metal sulfides which tend to remain with the solid bed. The desulfurized hydrocarbon product leaves the treating zone and is transported to an appropriate storage zone, cooling zone, or other processing step. When the flow of the hydrocarbon feed is upstream through the solid bed, it will be appreciated that the carbon monoxide formed by the decomposition of the carbonyl is admixed with the hydrocarbon product. In this case, the mixed product stream may be

handled in a conventional manner to separate the hydrocarbon components from the gaseous carbon monoxide. Thus, liquid hydrocarbons may be readily separated from the carbon monoxide by a simple phase separation technique. Vaporized hydrocarbons may be condensed by passage through a suitable cooling means and the resulting condensate then separated from the carbon monoxide by a simple phase separation procedure.

When the flow of the hydrocarbon stream is downflow through the catalyst bed and the desulfurized product is withdrawn from the bottom of the bed, it is apparent that no separation of the product from the carbon monoxide product will be necessary, since the latter product will conventionally be withdrawn from the top of the bed.

In any case, the hydrocarbon product may contain small amounts of finely divided metal, metal sulfides and the like. These insoluble constituents may be removed from the hydrocarbon product as by a conventional settling, filtration, centrifuging or other conventional separation procedure. Such techniques are familiar to those skilled in the art, and a detailed discussion of the techniques is not considered to be a vital part of the present description.

As the desulfurization reaction progresses, it follows that the bed of particulate solids gradually experiences an accumulation of the metallic products that are formed by the decomposition reaction and the desulfurization reaction. When the accumulation of such products has become so large as to impair the effectiveness and efficiency of the reaction and to interfere with the normal flow of the fluid streams involved, the reaction may be interrupted and the bed cleared of these metal products. It is apparent that the length of time that will ordinarily govern the point of interrupting the desulfurization reaction will depend upon the size of the reaction zone as well as the feed rate and sulfur content of the hydrocarbon feed stream. In most instances it is contemplated that a considerable reaction time will be available for the desulfurization step before a "regeneration" of the bed is required. At this point several procedures may be employed for this purpose. When the operation utilizes a fixed bed of particulate solids, the regeneration may take place directly within the treating zone; and a plurality of such zones may be obviously utilized to achieve substantially continuous operation. When the particulate solids are used in the form of a moving or fluidized bed, it is apparent that regeneration of the bed may be continuously conducted in a separate vessel or zone which is in substantially direct communication with the desulfurization zone. Details of this nature are well understood and appreciated by those skilled in the art.

Since it is contemplated that the best mode of operation for the present invention lies in the use of a fixed bed, the following description is directed toward a procedure for removing insoluble metallic and sulfur-containing materials from such a bed. As a first step in such a procedure, a solvent for the hydrocarbon constituents in the bed may be passed through the bed until such time as substantially all of the hydrocarbons present therein are removed from the bed. Suitable solvents for this purpose include other hydrocarbons generally less viscous and lower boiling than the hydrocarbon feed. Particularly desirable hydrocarbons for this purpose are hydrocarbons that boil up to about 400° F. and preferably up to about 250° F. Especially attractive hydrocarbons include pure hydrocarbons such as heptane, benzene, toluene and hydrocarbon mixtures such as light naphthas including virgin naphthas, catalytic naphthas and hydroformate naphthas. In any event, it is desirable that the solvents contain relatively little sulfur, preferably less than about 0.05 wt. per cent.

After the bed has been freed of residual hydrocarbon feed, steam, hot flue gas, or other substantially chemically inert vapors or gases may be passed through the bed at a temperature adapted to strip the solvent from the bed. Following this, carbon monoxide may be then introduced within the bed under conditions of temperature and pressure that are conventionally employed and recognized for converting metallic nickel and sulfides of nickel back to nicked carbonyl. Temperatures of 50 to 150° F. and pressures of 500 p. s. i. g. represent accepted conditions for this particular reaction.

A preferred embodiment of this invention is to employ caustic soda solution together with the carbon monoxide thereby providing accelerated means of decomposing the nickel sulfide formed. This is represented by the general equation as follows:

$$6NaOH + 2nNiS + 8nCO \rightarrow 2Na_2S_{n-1} + Na_2S_2O_3 + 3H_2O + 2nNi(CO)_4$$

The entire operation of desulfurization and regeneration of the surface necessary for successful desulfurization is more fully understood by reference to the attached drawing. Alternate reactors are depicted showing desulfurization in one reactor and surface regeneration in the other, but this does not limit the invention to two such vessels.

A portion of feed from line **2** is by-passed through line **4** from whence it goes through scrubber **10** where it picks up nickel carbonyl from a nickel carbonyl-carbon monoxide mixture from reactor **20'**. The feed containing the nickel carbonyl is passed through line **12** and into line **14** where it is blended with condensate flowing from gas separator **40** through line **48**. Any make-up nickel carbonyl is supplied through line **13**. The combined feed is passed through line **18** to reactor **20** where the carbonyl is decomposed and the desulfurization is effected in the presence of the particulate solid as described previously. Heat is supplied to the system by passing a portion of the feed through line **8** from heat exchanger or fired coil **6**.

The product from the desulfurization zone **20** passes through line **22** and line **24** to any convenient storage or stream. An alternate route is through line **22** and cooler **26** whence it is blended in line **28** with caustic solution from line **22'** and cooler **26'**. The combined streams pass through line **28** and may be augmented with condensate from gas separator **40** through lines **43** and **46**. The total combined streams pass through line **50** to settler **30**. Purified hydrocarbon is removed through line **31**. Spent caustic containing sodium polysulfide and sodium thiosulfate is removed through line **32**. When the purified oil is removed through line **24**, spent caustic is removed through line **24'**.

The gaseous product from reactor **20** which consists essentially of carbon monoxide and volatile hydrocarbons resulting from side reactions passes through lines **21**, **23**, **25**, cooler **27** and line **29** to gas separator **40**. The gaseous product from settler **40** passes through lines **41** and **45'** to reactor **20'** which previously had been cleared of polymer materials by solvent washing as discussed previously. The solvent is introduced through line **19'** and removed through line **22'** and **24'**.

Simultaneously with the carbon monoxide containing gas from **45'** which may be augmented with make-up carbon monoxide from line **47**, caustic soda is introduced through line **36'**. This stream consists of recycle caustic solution from line **34** and/or fresh caustic from line **35**. The caustic removal has already been discussed.

The gaseous product from reactor **20'** is a mixture of carbon monoxide and nickel carbonyl; and it is conducted through vapor lines **15'** and **17** to scrubber **10** where the nickel carbonyl is dissolved by a portion of the feed. The carbon monoxide leaves scrubber **10** through line **11** and is combined with that from line **23** which came from decomposition of nickel carbonyl in reactor **20**. The combined carbon monoxide stream passes through lines **25**, cooler **27** and line **29**, as already discussed, to sepa-

rator 40. Any purging is through line 43 and make-up carbon monoxide is introduced through line 47.

The simultaneous desulfurization and solid reactivation has been described. It is obvious to those skilled in the art that vessels 20 and 20' are used interchangeably. That is, when reactor 20 is used to the point of inefficiency it is cooled, flows are reversed and then reactor 20 takes the position of reactor 20' in the above description. Likewise reactor 20' assumes the position of reactor 20.

The present invention may be even better understood by reference to the following specific example in which a West Texas heavy gas oil containing about 1.6 wt. percent sulfur was treated in accordance with the process of this invention. This gas oil had an A. P. I. gravity of about 21 and a boiling range of about 650 to 950° F.

Samples of the gas oil were charged to an autoclave along with different amounts of activated charcoal and nickel carbonyl, alone and in combination with one another. The activated charcoal was a conventional coconut type of char having a particle size of about 3/16 inch diameter and a surface area of about 1000 square meters per gram. The nickel carbonyl, which is a low boiling liquid, was dissolved in the hydrocarbon feed prior to charging of the autoclave.

A series of runs were carried out using the above-mentioned materials; and the results of these runs are presented in the following table:

Run No.	Feed	I	II	III	IV
Grams, Act. Char		0	0	350	350
Grams Feed		500	500	490	500
Grams $(Ni(CO)_4$		75	75	75	75
Temperature, ° F.		795	700	700	700
Pressure, p. s. i. g. (Max.)		950	500	550	400
Hours of Run		4	4	4	4
Wt. percent S in Recov. Liq.	1.6	1.34	1.5	0.2	0.2

The ability of an activated char in combination with nickel carbonyl to desulfurize a hydrocarbon feed stock is apparent from the above table. It is further apparent that the combination affords a degree of desulfurization which is markedly superior to the moderately successful results that have been heretofore attainable with nickel carbonyl or activated char. The superiority of the combination over the carbonyl is immediately evident in the table itself.

It will be appreciated that the invention is not to be limited by this particular example. Rather, the example is intended merely to demonstrate the principles and effectiveness of the same. It will be understood that iron and cobalt carbonyls may also be utilized and that feedstocks and apparatus other than those mentioned in the example may be employed.

What is claimed is:

1. The method of desulfurizing a sulfur-containing mixture of hydrocarbons which comprises contacting the mixture in a treating zone with an iron group metal carbonyl in the presence of a particulate solid of large surface area and at a pressure and temperature adapted to decompose the metal carbonyl into the metal itself and carbon monoxide, maintaining said hydrocarbon mixture and said metal carbonyl within the treating zone for a period of about 0.5 to 5 hours, the total amount of said metal carbonyl being sufficient to provide at least 1 mol of said metal per mol of sulfur that is introduced within the zone, and withdrawing the desulfurized hydrocarbon mixture from the zone.

2. The method of desulfurizing a sulfur-containing petroleum fraction which comprises introducing the fraction within a treating zone which is substantially filled with a particulate solid possessing a surface area of at least about 100 square meters per gram, passing the fraction through the zone at a rate of at least 0.25 pounds of fraction per hour per pound of solid, introducing an iron group metal carbonyl within the treating zone in an amount sufficient to provide at least 1 mol of metal per mol of sulfur that is introduced within the zone, maintaining the zone at a temperature and pressure adapted to decompose the metal carbonyl into the metal itself and carbon monoxide whereby the metal reacts to remove sulfur from the fraction, and withdrawing the desulfurized fraction from the zone.

3. A method of desulfurizing a sulfur-containing petroleum fraction which comprises passing the fraction through a treating zone which is substantially filled with a particulate solid having a surface area of at least 100 square meters per gram at a rate of about 1 volume of fraction per hour per volume of solid, introducing an amount of nickel carbonyl within the treating zone so as to provide about 1 to 2 mols of nickel per mol of sulfur within said zone, maintaining the temperature of the zone at a value of about 600 to 800° F., whereby the nickel carbonyl decomposes to form a metallic nickel and carbon monoxide and the metallic nickel reacts with the sulfur-containing compounds in the petroleum fraction, withdrawing the carbon monoxide and desulfurized fraction from the treating zone and separating the desulfurized fraction from the carbon monoxide.

4. A method for desulfurizing a petroleum fraction which boils above about 750° and which contains more than about 0.3 wt. per cent sulfur which comprises contacting the fraction with an iron group metal carbonyl in a reaction zone in the presence of a particulate solid and at a temperature of 500–800° F. and a pressure of 300–900 p. s. i. g., the particulate solid being non-reactive with metal carbonyl and having a surface area of at least 100 sq. meters per gram, the feed rate of the petroleum fraction being from 0.5 to 2 liquid volumes per hour per volume of particulate solid, the amount of metal carbonyl introduced within the reactin zone being such as to provide at least one mol of metal per mol of sulfur in the petroleum fraction, maintaining the petroelum fraction within the reaction zone for a period of 0.5 to 5 hours whereby the metal carbonyl reacts to form metal sulfide with the sulfur in the petroleum fraction and carbon monoxide, withdrawing the desulfurized petroleum fraction and carbon monoxide from the reaction zone, and separating the desulfurized fraction from the carbon monoxide.

5. A process as defined in claim 4 in which the metal carbonyl is nickel carbonyl.

6. A process as defined in claim 5 in which the particulate solid is an activated clay.

7. A process as defined in claim 5 in which the particulate solid is an activated char.

8. A method as defined in claim 7 in which the feed rate of the petroleum fraction is about one liquid volume per hour per volume of char.

9. A process as defined in claim 8 in which the reaction temperature is about 700° F.

10. A method of desulfurizing a residual type petroleum fraction boiling above 750° F. and containing more than 1.0 wt. per cent sulfur which comprises passing the fraction at a rate of about 1 liquid volume per hour per volume of activated char through a bed of activated char at a temperature of about 700° F. and a pressure of about 500 p. s. i. g., said activated char containing an amount of nickel carbonyl sufficient to provide about 1 to 2 mols of nickel per mol of sulfur in the petroleum fraction and possessing a surface area of more than 500 sq. meters per gram, maintaining a portion of the petroleum fraction in contact with the activated char for a period of about 4 hours whereby the nickel carbonyl reacts with sulfur-containing compounds in the petroleum fraction to form compounds of nickel and sulfur and also carbon monoxide, withdrawing the resulting desulfurized

petroleum fraction and carbon monoxide from the reaction zone, separating the desulfurized fraction from the carbon monoxide, thereafter converting any nickel and nickel compounds in the activated char to nickel carbonyl by passing a hydrocarbon-type solvent through the activated char to remove hydrocarbons therefrom, adjusting the conditions of temperature and pressure within the activated char and passing an inert gas through the char to strip said solvent from the char, thereafter passing carbon monoxide through the char at a temperature of 50–150° F. at a pressure of about 500 p. s. i. g. to convert said nickel compounds to nickel carbonyl.

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