

April 12, 1960

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HYDROCRACKING OF HYDROCARBONS FOLLOWED
BY CATALYTIC CRACKING

2,932,611

Filed June 8, 1954

2 Sheets-Sheet 1

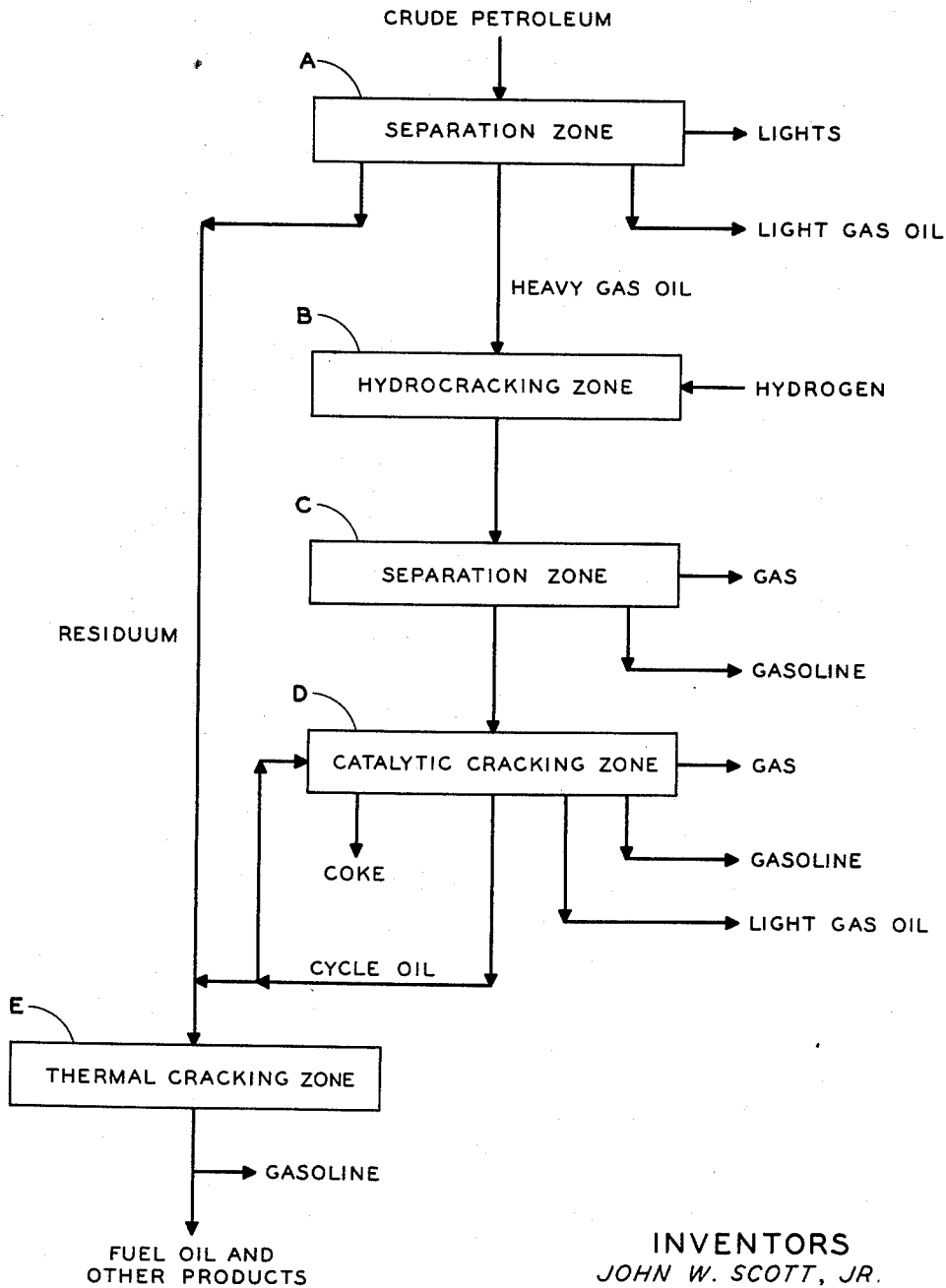


FIG.1

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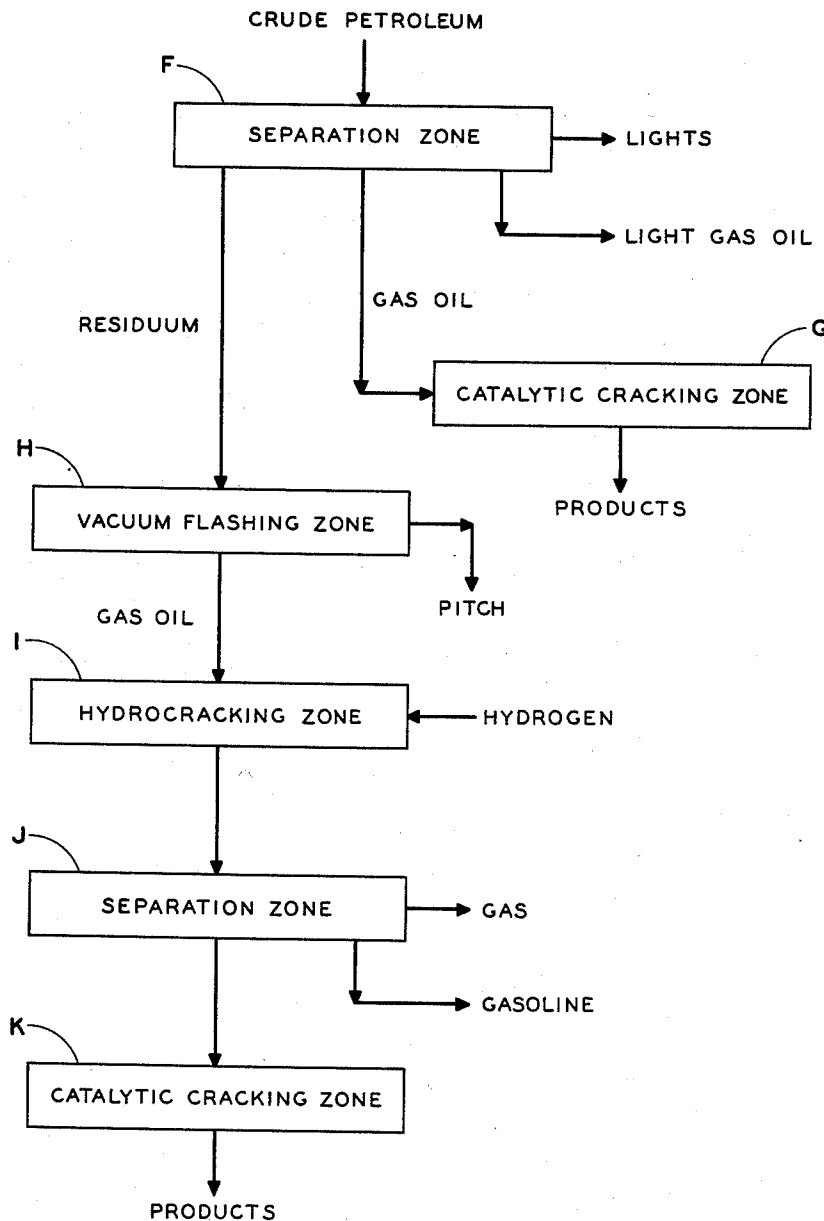


FIG. 2

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**PROCESS OF CATALYTIC DESULFURIZATION
AND HYDROCRACKING OF HYDROCAR-
BONS FOLLOWED BY CATALYTIC CRACK-
ING**

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Application June 8, 1954, Serial No. 435,164

2 Claims. (Cl. 208—94)

This invention relates to the catalytic cracking of petroleum hydrocarbons. More particularly, it relates to the treatment of petroleum hydrocarbons heavier than gasoline that contain sulfur and/or organo-metallic compounds prior to catalytic cracking so as to obtain increased yields of gasoline during cracking.

In the petroleum industry, the most important product is gasoline, and the primary aim is to produce the maximum quantity of gasoline of highest possible quality from a barrel of petroleum at the lowest possible cost. With the advent of the catalytic cracking process, improved yields of excellent quality gasoline were realized over that obtained prior to the development of this process. The best petroleum feed to a catalytic cracking unit has, over the years, been found to be a straight-run distillate oil of the nature of gas oil obtained from crude petroleum by simple distillation. However, the amount of feed stock of this nature is limited and the amount of residue fraction is large. Consequently, various methods have been devised for cutting more deeply into the residue fraction in order to obtain greater quantities of catalytic cracking charging stock.

There are two major problems encountered in the preparation of catalytic cracking feed stocks from residue fractions. The first is that such a feed stock must be relatively free of contaminants, particularly sulfur-containing and organo-metallic compounds. If sulfur compounds are present to any extent in the feed, the gasoline and other products from the catalytic cracking unit will also contain sulfur, which is undesirable. Organo-metallic impurities tend to poison the cracking catalysts, and thereby increase the cost of the operation by decreasing the useful catalyst life.

The second problem deals with the quality of the residue after removing the gas oil distillate intended as catalytic cracking feed stock. In order to realize full economic benefit from the crude petroleum, the residue is usually thermally cracked and then blended with other oil (called cutter stock) and sold as fuel oil. However, in order to sell this fuel oil, it must meet various specifications, particularly one of viscosity. It is generally most attractive to dispose of the residue as liquid fuel oil in this way; however, in some instances it may be coked for production of other products. From an economic standpoint, it is normally desired to produce the minimum amount of fuel oil and the maximum amount of gasoline, since fuel oil has a relatively low value as compared to gasoline. As the amount of catalytic cracking feed stock is increased by cutting deeper into the residue and reducing its production, the amount of cutter stock that must be blended into such residue to meet the viscosity specifications of fuel oil must also be increased. Therefore, the petroleum refiner must strike a balance of all these factors. Namely, he seeks to produce the maximum amount of catalytic cracking feed stock, bearing in mind the amount of contaminants in the feed and their effect upon subsequent operations, and the minimum amount of specification fuel oil which entails blending a minimum

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amount of cutter stock with the residue to meet the viscosity requirements of a salable fuel oil.

The cutter stock mentioned above is normally cracked gas oil, called cycle oil, from the catalytic cracking unit and is obtained by removing the cracked gasoline and lighter components from the product of the catalytic cracking unit. Therefore, it can be seen that if a deep straight-run gas oil cut is made in the crude distillation unit, and if this catalytic cracking unit feed is cracked to produce large quantities of gasoline, that the amount of cycle oil bottoms from the cracker may not be sufficient to reduce residual fuel viscosity to market specifications.

Insofar as the first problem noted above is concerned, i.e. contamination of the feed stock, it is known to desulfurize petroleum fractions by passing them in admixture with hydrogen over a sulfur-resistant hydrogenation catalyst at elevated temperatures and pressures whereby the sulfur present in the organic sulfur-containing compounds is converted to hydrogen sulfide which is then removed from the system. The hydrogen required to effect this conversion can be supplied either from an extraneous source or is derived from the feed stock itself as in the "autofining" process. However, the objective of such operations has been only to remove the sulfur, and the practice has been to employ the minimum temperature and pressure conditions which would effect this result.

The primary object of this invention is to provide an improved process whereby increased yields of gasoline and a smaller quantity of fuel oil of satisfactory quality may be obtained from a given quantity of petroleum. A further object is to provide an improved process for the removal of sulfur and organo-metallic compounds from petroleum distillates of the type employed as charging stocks to a catalytic cracking unit.

Numerous other objects will be apparent from a consideration of the following disclosure taken in conjunction with the accompanying drawings which diagrammatically illustrate alternative processes, each embodying the features of the present invention.

The present invention is based on the discovery that a major increase in the total gasoline production per barrel of the petroleum fraction conventionally employed as feed to a catalytic cracking unit, whether or not subjected to a prior hydrodesulfurization treatment of the type referred to above, can be realized by first catalytically hydrogenating the feed stock under conditions of temperature, pressure, and space velocity so as to effect substantial hydrocracking of the stock, and thereafter subjecting the higher boiling portion of the resulting hydrocracked product to a catalytic cracking treatment. In this sequence of operations it would normally be expected that the yield of gasoline produced as a result of the hydrocracking step would proportionately reduce the yield obtained in the subsequent catalytic cracking operation, particularly since it is known that a hydrocracked stock is much more refractory than stock not subjected to cracking conditions. However, it appears that the practice of the two steps in sequence, with intermediate removal of the gasoline and lighter fractions produced as a result of the hydrocracking step, has a synergistic effect whereby the total gasoline produced per barrel of feed stock is greatly increased over that which would otherwise be obtained either by a practice of the catalytic cracking step alone, or by the said step along with a prior mild hydrogenation (i.e. hydrodesulfurization) treatment of the type heretofore practiced in the art to remove sulfur from sulfur-containing feed stocks. Furthermore, as a result of the increased gasoline production, the heavy gas oil (cycle oil) from the catalytic cracking step is quantitatively less than that obtained from catalytic cracking of non-hydrocracked feed, but the viscosity is lower, thereby making it as least as effective as cutter stock as that obtained by only a catalytic cracking

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step. It has also been found that the hydrocracking step of the present invention not only effectively desulfurizes the stock to the catalytic cracking unit, but it also has the effect of removing any metal contaminants which may be present in the original feed stock before the catalytic cracking unit is reached. This metals removal is a result that is not accomplished to any appreciable extent in the ordinary hydrosulfurization processes heretofore noted.

As a result of this contaminant removal, a wider boiling range fraction of gas oil from a metals-containing crude petroleum can be employed as catalytic cracker feed, since in the past the boiling range of the feed stock was often dictated by the metals content due to the metals poisoning effect on catalytic cracking catalyst, the metals-containing compounds generally boiling with the heavier gas oils.

According to the present invention, hydrocarbon feed is reacted with hydrogen at a temperature in the range about 800 to 900° F., a pressure in the range about 300 to 1500 p.s.i.g., and a space velocity in the range about 0.8 to 5.0 v./v./hr. (liquid volumes of feed per volume of catalyst per hour), in the presence of a sulfur-resistant hydrogenation catalyst. Any organically combined sulfur in the feed is thus hydrogenated to hydrogen sulfide which is removed from the system. Any organo-metallic compounds are also hydrogenated resulting in the metals depositing upon the hydrogenation catalyst. The treated feed is then fractionally distilled and the gasoline and lighter components are removed as an overhead, and the bottoms fraction is passed to a conventional catalytic cracking unit where the fraction is catalytically cracked to produce substantially sulfur-free gasoline, cycle oils, and other products.

Some of the unexpected advantages realized by the present invention over the hydrosulfurization processes known in the art can be best pointed out by comparison. The conventional desulfurization is accomplished by contacting the feed with hydrogen in the presence of a hydrogenation catalyst such as cobalt-molybdate supported on alumina, at certain conditions of temperature, pressure, and space velocity. These conditions usually fall in the following ranges:

Temperature	-----° F.	600 to 775
Pressure	-----p.s.i.g.	100 to 500
Space velocity	-----v./v./hr.	0.5 to 10

Under these conditions, it has been found that sulfur contaminants will be removed to such an extent that the catalytic cracking product is not sulfur-contaminated to any great degree, and the gasoline product from the catalytic cracking unit is low enough in sulfur to be marketable. However, as noted before, these conditions will not hydrogenate any substantial amount of the organo-metallic compounds in the feed.

In the present invention, we have found that if the temperature and pressure are increased over the conventional hydrosulfurization process, that not only will the same result be obtained regarding sulfur hydrogenation and removal, but that due to the temperature and pressure increase, substantial hydrogenation of any organo-metallic compounds will be accomplished, and that hydrocracking will occur with the result that a gasoline is produced that is substantially free of sulfur. When the gasoline and lighter constituents produced in the treatment are removed by fractional distillation, the remaining hydrocarbon fraction will be substantially free of metals and sulfur and will also be more refractory toward catalytic cracking than the original feed, as might be expected. Despite the refractory nature of the fraction, when it is catalytically cracked, the gasoline produced in the catalytic cracking process is of higher quality than that produced directly from the original feed, and the cracking efficiency (gasoline/gas ratio and gasoline/coke ratio) is considerably improved over the case where the heavy gas oil is run through the catalytic cracking step without the hydrocracking treatment. Further-

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more, the heavy bottoms fraction from the catalytic cracking unit will be less in amount than if the feed was only catalytically cracked, which also might be expected, but contrary to what might be anticipated, the viscosity of these bottoms, if the present process is employed, is lower than that where there is no hydrocracking of the catalytic cracking unit feed, so that even though the amount is less, the viscosity is lower and can thus be used as cutter stock to blend with the crude residuum to produce a specification fuel oil. Thus, total gasoline (with an end point in the range about 375 to 425° F.) production per barrel of catalytic cracking unit feed stock has been found to be increased as much as 100 percent over that obtained in the past at the same fuel oil viscosity. It is important to emphasize that this increase in gasoline yield is possible without encountering viscosity limitations which, through their effect on fuel oil quality, usually limit the amount of gasoline which can be produced from a crude oil.

A further aspect of the present invention is the effect that the hydrosulfurization-hydrocracking treatment prior to catalytic cracking has upon metals-containing crude petroleum. Many crude oils contain organo-metallic impurities, with vanadium, nickel, copper and iron predominating. These metallic compounds, if present in catalytic cracking feed stock, will poison the cracking catalyst (silica-alumina or the like) with a resulting rapid decline in catalyst activity. It has been found that in order to prevent this rapid catalyst poisoning, the metals content of the cracking feed is desirably kept below 4 parts per million. Since the metallic compounds generally boil in the same range as the heavier gas oils, it is often required when treating metals-containing crudes, to reduce the upper limit of the boiling range of the gas oil catalytic cracker feed to exclude them. As a result, portions of the heavier gas oils, which are excellent catalytic cracker feed stock, cannot be employed as such due to the high metals content and must instead be removed with the residuum from the crude distillation column at an economic loss.

The present invention largely eliminates the above-noted problem in respect to metals-containing crude oils. According to the subject process, a heavy gas oil boiling range fraction including as much as 50 parts per million of metal in organo-metallic compounds may be employed as feed to the hydrocracking step. This is due to the fact that these metals do not poison the hydrogenation catalyst and that when the organo-metallic compounds are hydrogenated in this treatment, substantially all of the free metals are deposited upon the hydrogenation catalyst, and therefore do not pass over into the treated products. After the gasoline that is produced by hydrocracking is separated from the product, the latter is an excellent catalytic cracking unit feed stock containing well below 4 parts per million of metallic compounds. Thus, the economic loss occasioned by a narrow gas oil cut due to metallic compounds present in the heavy gas oil fraction is eliminated, because the metals are reduced in the hydrosulfurization-hydrocracking treatment to a point where they can be tolerated upon subsequent catalytic cracking. It should also be noted that, employing the process of the present invention, there is a certain amount of hydrogenation of organonitrogen compounds to ammonia with a resulting decrease in the content of undesirable nitrogen in the effluent from the hydrocracking step. About 40 percent of the nitrogen present in feed stocks is readily removed in this manner, the precise amount removed varying with the particular feed and catalyst combinations.

In the hydrocracking treating step of the present invention, the hydrocarbon feed stocks are reacted with hydrogen in the presence of hydrogenation catalysts (described below) by any suitable means. Any method of reacting a liquid, vapor, or mixed phase feed with hydrogen in the presence of a catalyst, either in a fixed bed, moving bed, or a fluid system of catalyst is operable.

The reaction between the hydrocarbon feed and hydrogen is one in which hydrogen is consumed. According to the present invention, hydrogen must be supplied to the reaction zone. In some of the ordinary low temperature hydrodesulfurization processes, hydrogen was also supplied due to hydrogen consumption during the reaction. However, we have found that despite the fact that the present invention involves both hydrodesulfurization and hydrocracking, the amount of hydrogen required to be added is approximately the same as that required in those processes wherein the hydrogen is employed for hydrodesulfurization alone. This is unexpected since the subject invention involves hydrocracking as well as hydrodesulfurization, and the answer appears to be that the feed stock itself furnishes the additional hydrogen requirements. We have found that hydrogen consumption is usually in the range 200 to 600 s.c.f./b. of feed (2 to 6 times the quantity of hydrogen stoichiometrically required to convert all of the sulfur contained in the feed to hydrogen sulfide), depending upon sulfur level and feed character. A hydrogen recycle in the range from 1000 to 10,000 s.c.f./b. of feed may be employed in the present process.

The reaction temperatures generally fall within the range 800 to 950° F., but the preferred range is 800 to 900° F., and a still more preferable range is from 825° F. to 875° F. At temperatures below about 775° F., very little hydrocracking occurs, and only the hydrodesulfurization of the stock results. At temperatures above about 900° F., the severity is so high that coke laydown on the hydrogenation catalyst occurs with the result that onstream periods are markedly reduced. Very high pressures are therefore required, and undesirable excessive hydrogenation, for example saturation of aromatic rings, can sometimes result. The temperature range of 800 to 900° F. provides excellent hydrocracking and sulfur-and-metallic compound hydrogenation along with only a small amount of coke laydown on the catalyst, affording reasonable onstream time, in the preferred range of moderate pressures, without a serious decline in catalyst activity. The more preferable range of 825 to 875° F. provides optimum results for carrying out the present invention.

The reaction is conducted in a pressure range of from 300 to 1500 p.s.i.g., with excellent results in the range 500 to 1000 p.s.i.g. and a preferred range of 800 to 900 p.s.i.g. At pressures below 300 p.s.i.g., little hydrocracking occurs, and the onstream period for the catalyst is prohibitively short due to coke laydown. At higher pressures, a tendency toward aromatics hydrogenation results in undesirably large hydrogen consumptions. The preferred ranges of pressure produce optimum results insofar as hydrocracking, coke laydown, and minimum hydrogen consumptions are concerned.

The space velocity within the hydrocracking step may be varied according to the degree of desulfurization and metals removal or the severity of the hydrocracking required, but in general should lie between 0.8 and 5.0 v./v./hr.

It has been found that if in the hydrocracking step the conversions to gasoline and lighter components are maintained in the range of from about 10 to about 40 volume percent, optimum conditions exist. That is, gasoline production will be thereby increased with excellent viscosity balance and cracking efficiency maintained throughout the process.

Suitable catalysts for use in the hydrocracking step are those known in the art as sulfur-resistant hydrogenation catalysts. Among these are metal sulfides and oxides, especially those of the 6th group, either alone (for example, chromium oxide and tungsten sulfide) or in admixture with other sulfides or oxide (for example, as pellets consisting of two parts tungsten sulfide with one part nickel sulfide) or in combination with other elements (for example, cobalt, nickel or iron) or mixed

with or deposited on a porous carrier such as natural or processed bauxite, activated alumina and kieselguhr. Cobalt, or cobalt-molybdate supported on alumina are good examples of hydrogenation catalysts. A cobalt-molybdate on a synthetic silica alumina cracking catalyst is particularly effective and produces a gasoline about 6 F-1 octane numbers higher than produced over the corresponding catalyst on an alumina support.

As hereinbefore noted, the product from the hydrocracking reaction zone is fractionally distilled to remove the gasoline and lighter components formed by hydrocracking, and the remainder of said product is catalytically cracked. The catalytic cracking operation may be performed in any process that is directed to that end. For example, it may be done in any of the conventional processes such as the fixed catalyst bed operation of the Houdry commercial units, or the Thermoform or fluid-type moving catalyst processes. As has been pointed out before, the treated feed to the catalytic cracking unit is on the refractory side compared to straight-run gas oil that is commonly used as feed to such a unit. However, cracking efficiency is improved and, of perhaps more importance, cycle oil viscosity is considerably reduced.

The process of the present invention is explained in the following description made with reference to the accompanying diagrammatic drawings.

Figures 1 and 2 show two different modifications of the invention.

Referring to Figure 1, the crude petroleum to be refined is passed into the first separation zone "A." In zone "A," which is normally a crude oil fractional distillation unit, separation into various fractions by their boiling point ranges is performed. The drawing indicates a separation into four major fractions: a light fraction that, in this description, includes kerosene and lighter components, among the latter being straight-run gasoline; a light gas oil fraction; a heavy gas oil fraction; and the residuum. The heavy gas oil fraction is conventionally employed as feed to a catalytic cracking unit, and it is here so employed. The heavy gas oil is passed from separation zone "A" to hydrocracking zone "B" where it is reacted with hydrogen over a hydrogenation catalyst as hereinbefore described. The products from zone "B" are passed into a second separation zone "C" where the gasoline and lighter components produced in the hydrocracking step are removed. The heavy fraction from separation zone "C" is then passed into the catalytic cracking zone "D" where it undergoes cracking. From zone "D" the product is removed and fractionated to yield conventional fractions, usually a light gas, C₃-C₄ hydrocarbons, gasoline, light gas oil, and coke. Portions of the cycle oil may be recycled to the catalytic cracking zone "D," and the remainder admixed with the residuum from separation zone "A" and passed through a thermal cracking zone "E" where it undergoes a thermal treatment. Among the products from zone "E" is fuel oil and gasoline.

Various modifications of the simple flow described above are as follows:

The straight-run gasoline produced in the first separation zone "A" may be sent to reforming facilities, such as thermal or catalytic reforming, or dehydrogenation, and the like. Since catalytic reforming or dehydrogenation processes produce hydrogen, they may be the source of hydrogen required in the hydrocracking zone "B." Likewise, the gasoline produced in the hydrocracking zone "B" and separation zone "C" may also be sent to a conventional catalytic reforming unit, i.e., hydroforming as described by Layng et al. in U.S. 2,270,715, or "Platforming" as disclosed by Haensel in U.S. 2,479,109, and the hydrogen produced there introduced into zone "B." Depending upon the relative amounts of gasoline to be reformed and gas oil to be hydrocracked, the whole operation may be self-sufficient as far as hydrogen is concerned.

Still another modification of the present invention is shown in Figure 2 and is particularly applicable when the crude petroleum employed is one in which there is a high organo-metallic compound content. As has been explained previously, the subject invention not only realizes increased gasoline production and sulfur removal, but also provides a means for the removal of metals so that these metals will not poison the catalytic cracking catalyst. It has been pointed out that the ability to remove these metallic compounds in hydrocracking zone "B" of Figure 1 allows a much broader boiling range of heavy gas oil to be used as catalytic cracker feed, since a metals content as high as 20 parts per million may be reduced to below 4 parts per million (a level which can be tolerated in catalytic cracker feed) in the hydrocracking zone. Utilizing the effect of metals removal, a modification of the process shown in Figure 2 takes advantage of the metals elimination and provides an excellent treatment for crude petroleum of high metals content. A metals-and-sulfur-containing crude oil feed is passed into separation zone "F" where, as in zone "A" of Figure 1, four fractions are separated from each other. A light fraction containing kerosene and lighter components and a light gas oil fraction are removed from the system and sent to conventional treating operations. A gas oil cut is also obtained, but the boiling range is narrower than the cut made in Figure 1, in that a metals content below 4 parts per million is maintained. Since this metals content is below the point at which catalytic cracking catalyst is poisoned, this fraction is passed directly to the first catalytic cracking zone "G." The residuum, containing the heavier gas oils and the organo-metallic constituents present in the crude petroleum, is passed into a vacuum flashing zone "H" where the residuum undergoes flash distillation under sub-atmospheric pressure. In zone "H," a heavy residue in the nature of pitch is removed from the system and generally passed to thermal cracking facilities, and the remaining petroleum composed of a fraction boiling in the gas oil range and containing, for example, 20 parts per million of metal (contained in organo-metallic compounds) is passed into a hydrocracking zone "I" where it is reacted with hydrogen in the presence of a hydrogenation catalyst. The product from zone "I," containing less than 4 parts per million of metals in organo-metallic compounds, is passed into the second separation zone "J," where the gasoline and lighter components produced in the hydrocracking step are removed. The heavy fraction from separation zone "J" is then passed into the catalytic cracking zone "K" where cracking occurs. From zone "K" the product is removed and fractionally distilled to yield conventional products.

An obvious modification of the process as shown in Figure 2 is to pass the heavy product from separation zone "J" directly to the first catalytic cracking zone "G," thereby eliminating cracking zone "K." Many other modifications which will be apparent to those skilled in the art are to be included in the scope of the invention. The following examples are presented to show the results obtained by the catalytic cracking of a given feed stock, both with and without the practice of a preliminary hydrodesulfurization step as heretofore employed in the art (Examples I and II) and then in Examples III and IV with the use of a preliminary hydrocracking step, as disclosed in the present invention. In each case the starting material employed as the feed had the following characteristics:

Southern California heavy gas oil	
Gravity, ° API	20.6
Pour point, ° F.	65
Viscosity (SSU):	
130° F.	129
210° F.	47.3
Initial boiling point, ° F.	385
End point, ° F.	1050
Sulfur content, weight percent	1.42

Metals content (parts per million):

Copper	1.5
Iron	4.5
Nickel	4.0
Vanadium	0.7

EXAMPLE I

In this operation, feed was passed directly to a catalytic cracking unit and cracked at a temperature of 900° F. over a silica-alumina cracking catalyst, there being employed a catalyst-to-oil volume ratio of 1.5 and a space velocity of 1.5 v./v./hr. A gasoline yield was obtained as follows:

Gasoline, st., 410° F., vol. percent	22.8
Gasoline sulfur content, weight percent	0.74

The heavy gas oil, or cycle oil, boiling above 410° F., from the cracking unit, has a viscosity of 44.5 SSU at 130° F.

EXAMPLE II

In this example, the feed stock was treated by a conventional hydrodesulfurization process under the following conditions:

The feed was passed to a hydrodesulfurization zone and reacted with hydrogen over a cobalt-molybdate hydrogenation catalyst at a temperature of 740° F., a pressure of 250 p.s.i.g., a space velocity of 2 v./v./hr., and a hydrogen recycle of 3800 s.c.f/b. of feed. The product was fractionally distilled and a gasoline yield was obtained as follows:

Gasoline, st., 410° F., vol. percent	3.7
Gasoline sulfur content, weight percent	.02

The product from the hydrodesulfurization contained the following metals, and the amount of each in parts per million.

Copper	0.3
Iron	3.4
Nickel	3.9
Vanadium	0.3

This effluent, after gasoline, was sent to a catalytic cracking zone where it underwent cracking conditions identical to those in Example I. The gasoline yield in volume percent, based upon the feed to the hydrodesulfurization zone and not on the feed to the catalytic cracking unit, was as follows:

Gasoline, st., 410° F., vol. percent	21.6
Gasoline sulfur content, weight percent	.28

The cycle oil from the catalytic cracking unit had a viscosity of 47.7 SSU at 130° F. The total gasoline produced, based upon the heavy gas oil feed to the hydrodesulfurization zone, was as follows:

Gasoline, st., 410° F., vol. percent	25.3
Gasoline sulfur content, weight percent	.24

EXAMPLE III

In this example, the feed stock was treated in general accordance with the method described above in connection with Figure 1. More specifically, the feed was passed to the hydrocracking zone "B" and reacted with hydrogen over a cobalt-molybdate hydrogenation catalyst at a temperature of 825° F., a pressure of 800 p.s.i.g., a space velocity of 2 v./v./hr., and a hydrogen recycle of 4340 s.c.v/b. of feed. The product was fractionally distilled and a gasoline yield was obtained as follows:

Gasoline, st., 410° F., vol. percent	18.0
Gasoline sulfur content, weight percent	0.014

The product from the hydrocracking zone contained the following metals, given in parts per million:

Copper	0.2
Iron	.95
Nickel	.09
Vanadium	.09

The product from the hydrocracking zone "B," after gasoline, was then sent to the catalytic cracking zone "D," where it underwent cracking operations identical to those in Examples I and II. The gasoline yield in volume percent based upon the feed to the hydrocracking zone "B" and not on the feed to the catalytic cracking unit, was as follows:

Gasoline, st., 410° F., vol. percent	17.4
Gasoline sulfur content, weight percent	0.028

Table I

	Example I	Example II	Example III	Example IV
Gasoline, Start, 410° F., Vol. percent	22.8	25.3	35.4	46.7
Gasoline Sulfur Content, Weight percent	0.74	.24	0.02	0.01
Percentage Sulfur Removal Based on Gasoline Sulfur and Feed Containing 1.42 Weight percent S	47.2	83.0	99.8+	99.8+

The percentage metals reduction of the feed stock to the catalytic cracking unit due to hydrogenation and deposition upon the hydrocracking catalyst is shown in Table II. The metals content (in parts per million) of the untreated feed is the same as that of Example I.

Table II

Metals	Example I		Example II		Example III		Example IV	
	Content (p.p.m.)	Percent Removal	Content (p.p.m.)	Percent Removal	Content (p.p.m.)	Percent Removal	Content (p.p.m.)	Percent Removal
Copper	1.5	0	0.3	80.0	.2	86.7	.01	99.4
Iron	4.5	0	3.4	24.5	.95	78.9	.6	86.7
Nickel	4.0	0	3.9	2.5	.09	97.8	.05	98.8
Vanadium	0.7	0	0.3	67.1	.09	87.1	.05	92.9

The viscosity of the cycle oil boiling above 410° F. was 45.2 SSU at 130° F.

Therefore, by employing the process of the present invention, the total gasoline produced based upon the heavy gas oil was as follows:

Gasoline, st., 410° F., vol. percent	35.4
Gasoline sulfur content, weight percent	0.02

EXAMPLE IV

The same conditions and procedure as Example III were employed in this example, except the hydrocracking temperature was 855° F., space velocity was 1.6 v./v./hr., and hydrogen recycle was 2600 s.c.f./b. of feed. The gasoline recovered from the hydrocracking step was as follows:

Gasoline, st., 410° F., vol. percent	35.3
Gasoline sulfur content, weight percent	0.004

The effluent from the hydrocracking step contained the following metals given in parts per million:

Copper	0.1
Iron	.6
Nickel	.06
Vanadium	.05

The product from the hydrocracking zone "B," after gasoline, was passed to catalytic cracking zone "D" and cracked under the same conditions as in Examples I, II, and III. The gasoline yield in volumes percent based upon the feed to zone "B" was as follows:

Gasoline, st., 410° F., vol. percent	11.4
Gasoline sulfur content, weight percent	0.04

The viscosity of the cycle oil, again boiling above 410° F. was 40 SSU at 130° F.

The combined gasoline production of Example IV was as follows:

Gasoline, st., 410° F., vol. percent	46.7
Gasoline sulfur content, weight percent	0.01

A comparison of the four examples is given below in Table I, and the increased gasoline production and the sulfur removal is evident.

As has been pointed out hereinbefore, the petroleum refiner seeks to produce the maximum amount of gasoline and the minimum amount of specification fuel oil which entails blending a minimum amount of cutter stock with the heavy residue to meet viscosity requirements of a salable fuel oil. The present invention allows the refiner to better accomplish this end than any other known process and this can best be shown by following the process of the subject invention according to Figure 2 when integrated with other refinery operations. The following examples show the treatment of the residuum from separation zone "F" to recover gasoline and specification fuel oil according to conventional methods and pursuant to the present invention.

EXAMPLE V

A Southern California residuum constituting 65.5 volume percent of the crude oil fed to separation zone "F" was removed from said zone, passed to vacuum flashing zone "H" where 61 volume percent of said residuum was separated as a gas oil catalytic cracking unit feed and the remaining 39 percent was a heavy residue or pitch. The gas oil fraction was then passed to a hydrodesulfurization zone corresponding to zone "I" under conditions identical to Example II above, i.e., 740° F., 250 p.s.i.g., space velocity of 2 v./v./hr., and a hydrogen recycle of 3800 s.c.f./b. The effluent from zone "I" was passed to catalytic cracking zone "K" where it underwent catalytic cracking. The cracked product from zone "K" was separated into two major fractions comprising gasoline and cycle oil (cutter stock), portions of the latter being recycled to zone "K."

The pitch from vacuum flashing zone "H" (39% of the residuum charged to zone "H") was admixed with the portion of the heavy cycle oil not recycled to catalytic cracking zone "K" and the admixture was passed to a thermal cracking zone where it underwent thermal decomposition. The effluent from the thermal cracking zone was then separated into gasoline and specification (viscosity 1250 SSU at 130° F.) fuel oil.

The over-all yields of gasoline, specification fuel oil,

and coke realized from the residuum charged to the vacuum flashing zone "H" were as follows:

Gasoline, acid treated to 0.25% sulfur, vol. percent	35
Specification fuel oil (viscosity, 1250 SSU at 130° F.), vol. percent	62
Catalytic cracking unit coke, wt. percent	2.6

EXAMPLE VI

In this example, the identical procedure of Example V was carried out, except that the 61 volume percent gas oil from vacuum flashing zone "H" was treated to more severe conditions in accordance with the present invention. The hydrocracking conditions were at 855° F., 800 p.s.i.g., space velocity of 2 v./v./hr. and a hydrogen recycle of 4000 s.c.f./b. The gasoline produced in the hydrocracking step was removed prior to catalytic cracking, but in all other respects the procedure followed Example V.

The over-all yields of gasoline, specification fuel oil coke from the residuum fed to vacuum flashing zone "H" were as follows:

Gasoline, .25% sulfur (no acid treating required), vol. percent	49
Specification fuel oil (viscosity, 1250 SSU at 130° F.), vol. percent	55
Catalytic cracking unit coke, wt. percent	1.1

A comparison of Examples V and VI shows that a 40% increase in low sulfur gasoline was realized employing the present invention with a corresponding 11% decrease in fuel oil of the same viscosity. Also, coke production was reduced appreciably.

We claim:

1. A process for obtaining increased yields of gasoline from crude petroleum containing sulfur and organo-metallic compounds which comprises fractionally distilling said crude petroleum to obtain a gas fraction, a gasoline fraction, a light gas oil fraction, a heavy gas oil fraction containing less than 4 parts per million of metals contained in organo-metallic compounds, and a residuum containing more than 5 parts per million of metals contained in organo-metallic compounds, passing said heavy gas oil fraction to a catalytic cracking zone and contacting it with a cracking catalyst under cracking conditions, passing said residuum into a vacuum flashing zone and there subjecting said residuum to flash distillation under sub-atmospheric pressure, removing from said flash distillation zone a heavy bottoms fraction and an overhead fraction composed essentially of hydrocarbons boiling in the

gas oil range and containing from about 5 to 50 parts per million of metal, contained in organo-metallic compounds, passing said overhead fraction into a hydrocracking zone and reacting it with hydrogen in the presence of a sulfur-resistant hydrogenation catalyst at a temperature in the range about 800 to 900° F., a pressure of from 300 to 1500 p.s.i.g., and a space velocity in the range about 0.8 to 5.0 v./v./hr., fractionally distilling the effluent from the hydrocracking zone containing less than 4 parts per million of metals to separate a fraction comprising gasoline and a higher boiling fraction, contacting said higher boiling fraction with a cracking catalyst in a cracking zone under cracking conditions, and recovering a gasoline fraction from the effluent of the cracking zone.

2. A process for obtaining increased yields of gasoline from crude petroleum containing sulfur and organo-metallic compounds which comprises fractionally distilling said crude petroleum to obtain a gas fraction, a gasoline fraction, a light gas oil fraction, a heavy gas oil fraction containing less than 4 parts per million of organo-metallic compounds, and a residuum containing more than 5 parts per million of organo-metallic compounds, passing said residuum into a vacuum flashing zone, where said residuum undergoes flash distillation under sub-atmospheric pressure, removing a heavy bottoms fraction from said flash distillation zone and an overhead fraction composed essentially of hydrocarbons boiling in the gas oil range and containing about 5 to 50 parts per million of metals contained in organo-metallic compounds, passing said overhead fraction into a hydrocracking zone and reacting it with hydrogen in the presence of a sulfur-resistant hydrogenation catalyst at a temperature in the range about 800 to 900° F., a pressure from 300 to 1500 p.s.i.g., and a space velocity in the range about 0.8 to 5.0 v./v./hr., fractionally distilling the effluent from the hydrocracking zone containing less than 4 parts per million of metals to separate a fraction comprising gasoline and a higher boiling fraction, admixing said higher boiling fraction with the heavy gas oil fraction and passing the admixture to a catalytic cracking zone and contacting it with a cracking catalyst under cracking conditions.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,932,611

April 12, 1960

John W. Scott, Jr., et al.

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

Column 12, lines 21 and 23, after "million of", each occurrence, insert -- metals contained in --.

Signed and sealed this 25th day of October 1960.

(SEAL)

Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents