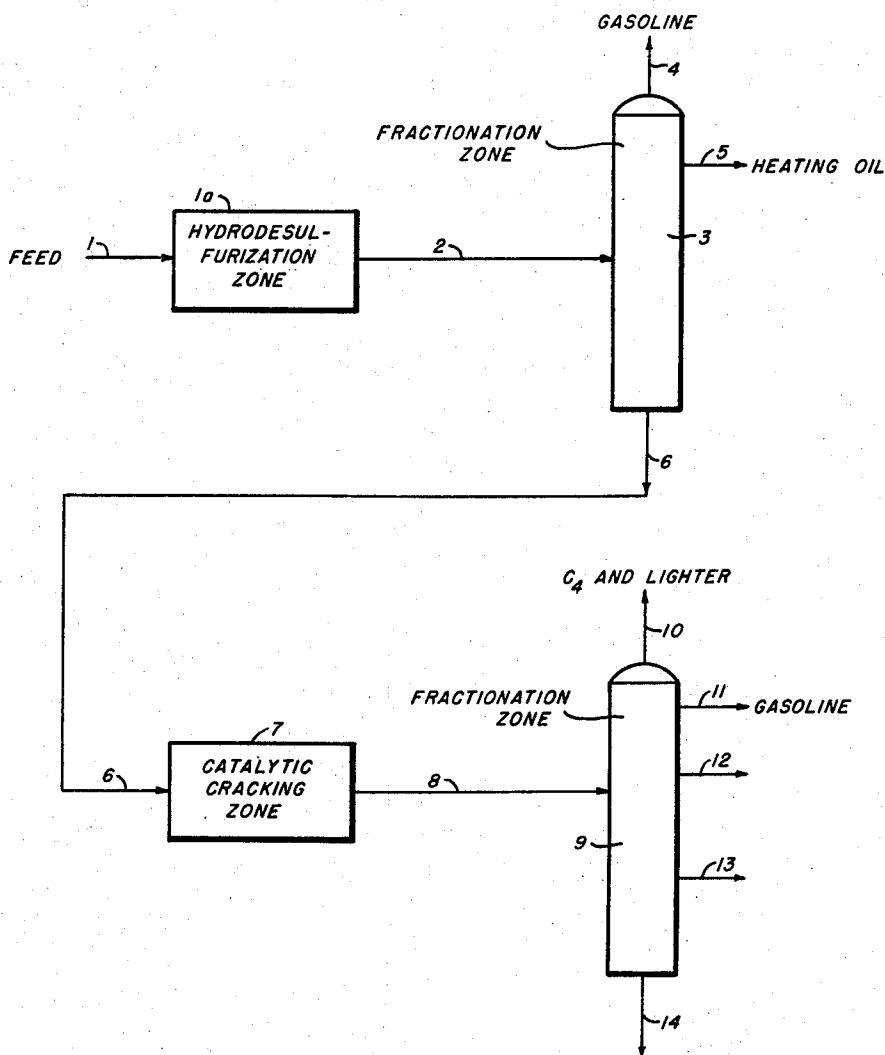


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CATALYTICALLY CRACKING GAS OIL
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1

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PROCESS FOR HYDRODESULFURIZING AND SUBSEQUENTLY CATALYTICALLY CRACKING GAS OIL

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This invention relates to the production of high quality gasoline by catalytic cracking of relatively high molecular weight hydrocarbons. The invention is particularly concerned with provision of low sulfur content catalytically cracked gasolines. In accordance with this invention the feed stock to a catalytic cracking operation is subjected to a hydrodesulfurization process with a desulfurization catalyst of improved physical characteristics in a manner providing marked advantages in the process and products of catalytic cracking.

At fairly recent dates it has become appreciated that the sulfur content of gasoline is much more important than formerly thought. It has now been established that extremely low sulfur contents are desirable particularly in order to reduce what is called the octane requirement increase of an engine. Gasolines which have been commonly used heretofore even though being considered to have satisfactory sulfur contents by the doctor test or the like have been found to be characterized by a marked increase in the octane requirement of an engine after extended use of the engine. One of the factors found to contribute to this is the sulfur content of the gasoline. It appears necessary and desirable to attain extremely low sulfur contents to avoid this problem. Attainment of low sulfur content gasolines is again important in order to improve the lead susceptibility of the gasoline to cause decreased engine wear and so on.

A potentially attractive process for attaining low sulfur content catalytically cracked gasolines is to first desulfurize the feed stock to the catalytic cracking operation. The feed stock is ordinarily the gas oil fraction of a petroleum crude oil boiling in the range of about 600 to 1000° F. or somewhat higher. The feed stock to catalytic cracking may also be reduced crude petroleum or a residual fraction such as a deasphalted residuum, boiling in the range from about 800° F. and higher. While the sulfur content of such a cracking feed stock will vary depending upon its source, in general such stocks will contain about 0.2 to 3.0% sulfur and typically will contain about 2% of sulfur. Heretofore it has not been the practice to desulfurize such feed stocks prior to catalytic cracking with the result that during cracking sulfur present in feed stock is in part converted to constituents of the final catalytically cracked gasoline. In general, the sulfur content of a catalytically cracked gasoline will be about 5–10% of the sulfur content of the cracking feed stock.

One of the most attractive possibilities for economically desulfurizing catalytic cracking feed stock employs the so-called hydrodesulfurization process. In this process the feed stock is contacted with hydrogen in the presence of a hydrogenation catalyst such as a cobalt molybdate catalyst supported on alumina. Effective desulfurization of gas oil is possible in this manner. However, the possibility of processing a gas oil or higher boiling fraction in this manner prior to catalytic cracking has never attained commercial usage because of se-

2

vere debits resulting from the process. A particular difficulty concerns the undesired hydrocracking of feed stocks during the hydrodesulfurization operation. This hydrocracking results in conversion of constituents of the feed stock boiling in the gas oil boiling range to cracked constituents boiling below the gas oil boiling range. Specifically, hydrocracking during hydrodesulfurization results in the formation of gasoline and heating oil fractions. With reference to the gasoline formed during hydrocracking, this gasoline is of substantially the quality of virgin naphtha and consequently much inferior to the superior quality high octane number gasoline obtainable by catalytic cracking. It is apparent then that any hydrocracking occurring during hydrodesulfurization of a cracking feed stock effectively results in loss of valuable feed for catalytic cracking in a commercially expensive manner. It is, therefore, the particular object of this invention to provide a hydrodesulfurization process which will substantially reduce hydrocracking during the hydrodesulfurization of a feed stock to be subjected to catalytic cracking.

It may be noted that in addition to the formation of products lighter than the feed due to hydrocracking, a small amount of lighter material is formed due to the desulfurization itself. That is, where a sulfur atom is connected to two hydrocarbon radicals in a molecule, removal of the sulfur will convert the molecule into two lighter hydrocarbon fragments. The amount of lighter products formed in this manner is, however, relatively insignificant.

The general nature and objectives of this invention can be understood by reference to the following specific data. In tests which were conducted to evaluate the production of catalytically cracked gasoline from a hydrodesulfurized gas oil, hydrodesulfurization was carried out using an active commercial desulfurization catalyst. The catalyst employed was a conventional cobalt molybdate catalyst supported on gamma alumina and activated at a temperature of about 1200° F. for a period of about 6 hours. This catalyst was employed to hydrodesulfurize a heavy West Texas gas oil having a sulfur content of 1.6%. The hydrodesulfurization conditions were 0.15 v./v./hr., 500 to 850 p.s.i.g., 735 to 750° F. and 6000 standard cubic feet of hydrogen per barrel. Inspection data of the gas oil fraction employed in these hydrodesulfurization experiments are given below:

Table I

	Virgin Gas Oil	Desulfurized Gas Oil
Bomb Sulfur, Wt. percent.....	1.6	0.13
Gravity, ° API.....	22.8	31.0
Aromatic Index.....	20	9
Conradson Carbon, Wt. percent.....	0.25	0.02
ASTM 50% Point, ° F.....	858	815

During attainment of the desulfurized gas oil indicated, hydrocracking occurred resulting in the formation of 9.4 volume percent of naphtha and 16.6 volume percent of heating oil. Segregating these fractions permitted a yield of 77.9 volume percent of the desulfurized gas oil characterized in Table I.

The desulfurized gas oil was then subjected to a catalytic cracking operation carried out by the fluidized solids technique. The cracking catalyst employed was a conventional silica alumina catalyst and the conditions of

3

cracking were conventional. In a first case the undesulfurized virgin gas oil employed in the above experiments was subjected to catalytic cracking, while in a second case the desulfurized gas oil referred to above was catalytically cracked. Summarized below are the yields of products obtained by employing these two feed stocks. These yields are compared on the basis of constant carbon burning rate during the catalytic cracking operation:

Table II

	Direct Cracking	Desulfurized Cracking
430° F. Conversion, Vol. Percent (Cat. Cracking Only)	50.0	57.3
Yields, Percent on Feed:		
Carbon, Wt. Percent	1.8	1.8
Dry Gas, Wt. Percent	7.5	8.0
Butylenes, Vol. Percent	8.7	9.4
Butanes, Vol. Percent	3.7	6.8
C ₆ -430° F. Naphtha—		
Desulfurized, Vol. Percent		9.4
Catalytic, Vol. Percent	37.9	29.1
Total Naphtha, Vol. Percent	37.9	38.5
430°-650° F. Heating Oil:		
Desulfurized, Vol. Percent		16.6
Catalytic, Vol. Percent	13.9	7.9
Total Heating Oil, Vol. Percent	13.9	24.5
650° F. + Cycle Stk., Vol. Percent	36.1	25.4

It will be observed from Table II that the undesired hydrocracking of the gas oil during hydrosulfurization resulted in a substantial decrease in the amount of catalytically cracked gasoline obtainable. Thus, on desulfurization of the gas oil followed by catalytic cracking a yield of catalytic naphtha of only 29.1 volume percent was obtained. As compared to this, a yield of catalytic gasoline amounting to 37.9% was obtainable by the direct catalytic cracking of the undesulfurized gas oil feed. It is apparent then that the conversion of gas oil constituents to naphtha constituents during hydrosulfurization resulted in reducing the yields of catalytic gasoline by an amount substantially equal to the gasoline formed by hydrocracking.

This factor is of great importance from a practical viewpoint because the gasoline formed during hydrosulfurization by hydrocracking is greatly inferior to catalytically cracked gasoline. For example, the hydrocracked gasoline obtained as indicated above only had a CFR research number of 69.7 when tested with 1.5 cc. per gallon of tetraethyl lead. As compared to this, the catalytic gasoline obtained as indicated has a CFR research number of 98.6 when tested with 1.5 cc. per gallon of tetraethyl lead. It must be appreciated then that the hydrocracked gasoline formed during a hydrosulfurization operation is of such unsuitable quality that the amount of this gasoline formed must be considered a debit for the process.

In other words, as brought out, in a combination process involving hydrosulfurization of a gas oil followed by catalytic cracking of the gas oil it becomes important to minimize hydrocracking during the first step. As pointed out, gasoline formed during desulfurization is of such poor quality that the formation of this gasoline results in the substantial loss of equivalent amounts of catalytically cracked gasolines. Another way of considering this is to appreciate that from a given gas oil feed stock a certain amount of gasoline can be obtained. Because of the superior gasoline obtainable by catalytic cracking, it is most attractive that all gasoline conversion be achieved by catalytic cracking. It is the particular

4

feature of this invention to provide a process which will permit the substantial attainment of this goal.

The present invention is based in part on the discovery that particularly effective catalysts for the hydrosulfurization of gas oil and heavier oils can be provided by controlling the physical characteristics of conventional porous solid desulfurization catalysts to maintain the following values: (1) A "most frequent pore diameter" (D_f) of the catalyst of at least about 60 Angstrom units and no greater than about 400 A. Preferable values are in the range from 75 A. to 200 A. (2) A spread of at least about 10 A. in the range of the more frequent pore diameters (ΔD_R); the spread is preferably in the range from 10 A. to 200 A. (3) A pore size distribution factor,

$$PD = \frac{(D_f)^2 \Delta D_R}{10^4}$$

of at least about 5, and preferably above 10.

The methods of determining D_f , ΔD_R and PD factor, and methods of preparing porous catalysts having controlled physical characteristics in the ranges set out above are described in detail in co-pending application Serial No. 490,732, now U.S. Patent No. 2,890,162, entitled "Improved Porous Contacting Agents and Use Thereof," filed of even date herewith in the names of James A. Dinwiddie, Max A. Mosesman, James A. Anderson, Jr., and Lonnie W. Vernon, the disclosures of which are made a part hereof.

The chemical nature of the preferred catalyst for the hydrosulfurization step of the present invention is, as described above, cobalt molybdate on alumina. This also embraces compositions of non-stoichiometric proportions of mixed oxides of cobalt and molybdenum on an alumina base. Such catalyst compositions are well known to the art. It is essential for the successful practice of the present invention that the hydrosulfurization catalyst have the physical characteristics set out above. Catalysts of other compositions than cobalt molybdate on alumina may suitably be employed, provided they have the physical characteristics set out, and have the chemical characteristics of desulfurization catalysts. Such catalysts are, for example: nickel or a compound thereof on alumina, platinum on alumina, and cobalt molybdate on other suitable supports such as zirconia or boria-alumina.

A preferred catalyst for use in the desulfurization step of the present invention may be prepared from conventional cobalt molybdate on alumina catalysts by heating these catalysts for a period in the range from about 4 to 36 hours at temperatures in the range of 1350° to 1550° F. A preferred range is between 1400 and 1500° F. It is to be understood that this particular heat treatment is carried out in addition to those conventionally applied to such catalysts during catalyst preparation. The results obtainable by heating the catalysts at the above defined conditions are not obtainable even at prolonged heating periods at temperatures in the conventional activation range of about 1000 to 1200° F.

Activation of these catalysts at temperatures above 1350° F. for periods of about 4 to 36 hours results in a substantial change in the physical characteristics of the catalysts. It has been established that the principal physical changes involve a substantial increase in the size of the most frequent pores of the catalyst and also a substantial broadening of the range in predominant pore sizes. Basic work has also established that these changes in physical properties markedly improve the activity and other catalytic properties of these catalysts.

A cobalt molybdate on alumina catalyst with the stated physical characteristics has been found to be particularly satisfactory for the hydrosulfurization of feed stock for

catalytic cracking. The special properties of the catalyst result in substantially minimizing the undesired hydrocracking ordinarily occurring during hydrodesulfurization. These properties of the catalysts are further utilized in accordance with this invention by employing particular temperatures of hydrodesulfurization and by conducting the process at particular rates of throughput.

The gas oil designated as feed stock No. 1 was then hydrodesulfurized in separate runs, employing catalysts A, B and C respectively, at a temperature of 765° F., a pressure of 400 p.s.i.g., a hydrogen feed rate of 6000 standard cubic feet per barrel, and several space velocities. Pertinent data regarding the catalysts and the hydrodesulfurization operations are shown in Table IV:

Table IV

Catalyst	A			B			C			
Heated 24 Hrs. at ° F.	1,100			1,400			1,500			
D _r , A.	35			60			114			
ΔD _R , A.	10			38			12			
PD Factor	1			14			16			
Conditions:										
Feed Rate, v./v./hr.	.23	.64	1.10	.24	.65	1.12	1.73	.25	.73	1.1
H ₂ /oil ratio, s.c.f./bbl.	6,250	6,810	6,870	5,790	6,520	6,090	6,450	6,010	5,820	6,230
Reactor Temperature, ° F.	765	765	765	765	765	765	765	765	765	765
Liquid Yields and Inspections:										
Vol. Percent Yield—										
Gasoline (boiling below 430° F.)	13.5	8.0	6.5	12.5	9.0	6.0	5.5	9.5	6.8	3.5
Heating Oil (boiling 430°–580° F.)		14.0	9.0	17.5	12.5	12.5	8.0	14.5	9.7	10.0
Gas Oil		77.5	83.2	67.9	77.9	79.8	86.6	75.1	82.0	85.5
Total	99.2	99.5	98.7	97.9	99.4	98.3	100.1	99.1	98.5	99.0
Wt. Percent Sulfur in liquid	0.04	0.10	0.17	.02	.06	.10	.16	.03	.09	.13
Sulfur removal, percent	97	94	90	99	97	94	91	98	95	93

These and other features of the invention will be established by the examples and data which follow.

In a first series of studies to evaluate the principles of this invention, separate portions of a cobalt molybdate type catalyst supported on low silica granular gamma alumina were subjected to activation at temperatures in the broad range of 1100 to 1500° F. for a period of 24 hours. The catalyst employed contained 15% of cobalt molybdate and was pilled in the form of 1/8 inch pills employing 3% graphite as a pilling aid. Prior to the extended activation at temperatures in the range indicated, this catalyst had been activated by treatment at 1200° F. for 6 hours. The portion activated for 24 hours at 1100° F. is hereafter referred to as catalyst A, that heated at 1400° F. as catalyst B, and that heated at 1500° F. as catalyst C. These catalysts were employed to hydrodesulfurize a West Texas gas oil designated as "feed stock No. 1" having the inspections shown in Table III:

Table III

Feed Stock	No. 1		No. 2	
Sulfur, Wt. Percent	1.72		2.10	
Gravity	24.1		24.4	
Distillation	ASTM		ASTM	
	Atmospheric	10 mm. Corrected to 760 mm.	Gas Oil Engler	10 mm. Corrected to 760 mm.
IBP, ° F.	471			
4.3% off at, ° F.	580			
5.	589	588	580	
10.	637	668		594
17.	650			
20.	670	713		657
22.			650	
30.	692	738		704
34.5.	700			
40.		769		740
50.		807		780
60.		846		817
70.		884		860
80.		925		903
90.		977		959
95.		1011		1005
FBP, ° F.		1032		

It will be noted from the data in Table IV that activation of a cobalt molybdate type catalyst at temperatures in the range of 1400° F. and higher results in catalysts having increased D_r, ΔD_R, and pore distribution factors, and improved properties for a hydrodesulfurization process. In particular it will be observed that activation at the high temperatures indicated causes a substantial increase in the hydrodesulfurization activity of the catalyst, indicating the permissible use of substantially higher throughput rates while attaining the same levels of desulfurization. Again the extent of hydrocracking encountered during hydrodesulfurization is shown to be critically affected by the change in physical characteristics of the catalyst. This is particularly shown by the data of Table IV with reference to the volume percent of gasoline yield. Thus, for example, at feed rates of about 1 v./v./hr. approximately 6.5% of constituents are converted to gasoline boiling range products by catalyst A, which was activated at 1100° F. and had a D_r of less than 35 A., ΔD_R of less than 10, and pore distribution factor less than 1. However, for catalyst C, activated at 1500° F. and having a D_r of 119 A., ΔD_R of 12 and pore distribution factor of 16, only about 3.5% of such conversion occurred. It is apparent then that a catalyst of increased pore size, pore size range, and pore distribution factor, such as the severely activated cobalt molybdate catalyst, permits attainment of increased desulfurization without a corresponding increase in hydrocracking.

Additional runs were then conducted to determine optimum conditions for hydrodesulfurization.

Two sets of runs were made to determine the temperatures suitable for hydrodesulfurization.

In the first set of runs the catalyst employed was the severely activated cobalt molybdate on alumina catalyst "C" described supra. The feed stock employed was the gas oil designated as feed stock No. 1, supra. The hydrodesulfurization processes were conducted at liquid space velocities of about 4.5 v./v./hr. at a pressure of 400 p.s.i.g. using about 6200 standard cubic feet of hydrogen per barrel of feed and employing as temperatures

of operation 765° and 797° F. The data obtained in these runs are summarized in table V-A:

Table V-A

Feed Stock.....	No. 1	
Catalyst.....	C	
D _r	114	
ΔD _r	12	
PD Factor.....	16	
Operating conditions:		
Space Velocity, v./v./hr.....	4.47	4.46
H ₂ /Oil Ratio, s.c.f./bbl.....	6,200	6,222
Pressure, p.s.i.g.....	800	800
Temperature, °F.....	765	797
Liquid Product Yields and Inspections:		
Engler Distillation—		
Vol. percent off:		
at 430° F.....	1.5	5.0
at 580° F.....	7.5	14.0
at 650° F.....	17.0	—
Wt. Percent Sulfur in Liquid.....	0.31	0.29
Sulfur Removed, Percent.....	82	83

It will be observed from the data in Table V-A that the temperature of operation between 765° and 797° F. did not significantly affect the extent of desulfurization, but that the amount of gasoline produced, indicated by the percent of liquid product distillable at 430° F., increased from 1.5% to 5%, and the amount of light heating oil, distillable from 430° F. to 580° F., increased from 6% to 9%, as the temperature was increased.

The second set of runs was made at temperatures in the range from 507° F. to 749° F. The catalyst employed, designated as catalyst "D," was a cobalt molybdate on alumina catalyst prepared from a commercial-type catalyst containing approximately 15 weight percent cobalt molybdate supported on substantially silica free alumina, in the form of ¼ inch pills, which had been heat-treated for six hours at 1200° F., ground, and re-pilled as ½" x ⅛" pills. The ½" x ⅛" pills were heated in the presence of moving air at a temperature of 1500° F. for 24 hours followed by crushing and screening to obtain catalyst "D" in the form of 10–20 mesh particles. The feed stock employed was a West Texas Gas Oil designated as Feed Stock No. 2, the inspections of which are given in Table III.

The hydrodesulfurization processes were conducted at liquid space velocities of about 2 v./v./hr., at a pressure of 800 p.s.i.g., using about 2100 standard cubic feet of hydrogen per barrel of feed, and employing various temperatures of operation in the range from 500° to 750° F. The data obtained in these runs are summarized in Table V-B.

It will be observed from the data in Table V-B that under the conditions of pressure and space velocity employed, the operating temperature did affect the degree of desulfurization. Substantial desulfurization was obtained at a temperature of 605° and higher. It will be further observed that the amount of gasoline produced, indicated by the percent of liquid product distillable at 430° F., increased from 1% at 605° F. to 5% at 749° F.; the amount of light heating oil produced indicated by the percent of product distillable between 430° and 580° F. less the 5% contained in the feed, increased from 5% at 605° to 8% at 749° F.; and the net change in the amount of heavier heating oil indicated by the percent of product distillable between 580° and 650° F. less the 17% contained in the feed, increased from a net disappearance of 5% at 605° F. to a net increase of 2% at 749° F.

Further comparing the runs in Tables V-A and V-B, the following may be noted: The reaction condition for the runs in Table V-B, including a lower space velocity, higher pressure, and lower hydrogen to oil ratio, were somewhat more severe than those in Table V-A. The catalysts were chemically identical, had received similar heat treatment and had similar pore distribution characteristics, but were dissimilar in that catalyst C was in the form of ⅛" x ⅛" pills and catalyst D was in the form of 10–20 mesh particles. It is believed that the catalytic effects of catalysts C and D were substantially identical. The feed stocks were chemically similar, being fractions of West Texas Crude, but feed stock No. 2 had a somewhat higher concentration of lower boiling components than feed stock No. 1.

The data in Tables V-A and V-B indicate that at the conditions and with the catalysts shown, substantial desulfurization of gas oil is obtained at temperatures in the range from 600° to 800° F., and that cracking of the gas oil is substantially reduced or almost totally inhibited at the lower temperatures in that range, especially between 600° and 765° F.

Additional runs were carried out in which gas oil feed stock No. 1 was hydrodesulfurized with catalyst "C" at 765° F., 400 p.s.i.g., with a hydrogen rate of about 6000 s.c.f./bbl. but in which the throughput of the operation was varied in the range of about 0.5 v./v./hr. to about 4.5 v./v./hr. In these experiments it was found that the amounts of hydrocracking occurring during hydrodesulfurization is very greatly affected by the throughput rate. It is apparent, of course, that the extent of desulfurization is also affected by throughput rate but the significant fact discovered was that the extent of hydrocracking could be substantially decreased at higher throughput rates without greatly affecting the degree of

Table V-B

Feed Stock.....	No. 2				
Catalyst.....	D				
D _r	90				
ΔD _r	30				
PD factor.....	24				
Conditions:					
Space Velocity, v./v./hr.....	2	2	2	2	2
H ₂ /oil ratio, s.c.f./bbl.....	2,100	2,100	2,100	2,100	2,100
Reactor Pressure, p.s.i.g.....	800	800	800	800	800
Avg. Reactor Temp., °F.....	507	605	652	677	749
Engler Distillation—					
Vol. percent off—					
at 430° F.....	trace	trace	1	2	5
at 580° F.....	5	11	12	12	18
at 650° F.....	22	23	27	30	37
Wt. Percent Sulfur in Liquid.....	2.10	1.81	1.18	0.57	0.28
Sulfur Removed, Percent.....	—	14	44	73	87

hydrodesulfurization. This effect is particularly indicated by the data shown in the following table:

Table VI

	CoMoO ₄ -Al ₂ O ₃ Catalyst Activated at 1,400° F.			
Space Velocity, v./v./hr.	0.5	1.0	1.5	4.5
Gasoline Yield, Vol. Percent	9	5.5	4.5	1.5
S in Product, Wt. Percent	0.05	0.10	0.20	0.31
Sulfur Removed, Percent	97	94	88	82

As developed, therefore, the process of this invention concerns the hydrodesulfurization of a gas oil or heavier essentially hydrocarbon fraction to be used as a catalytic cracking feed stock under the following specific conditions: the catalyst employed is a porous solid desulfurization catalyst having a most frequent pore diameter, D_p , of at least 60 Å. and preferably in the range from 75 Å. to 200 Å. a spread in more frequent pore diameters, ΔD_p , of at least about 10 Å. and preferably between 10 Å. and 200 Å. and a pore distribution factor, PD, of at least 5. The throughput employed is to be in the general range of about .5 to 6 v./v./hr. and preferably well above 1 v./v./hr., e.g. in the range from 2 to 4.5 v./v./hr. The amount of hydrogen employed may be chosen from the range of about 1000 to about 6500 cubic feed per barrel depending in part on the sulfur content and nature of the feed stock to be hydrodesulfurized. The hydrogen rate may be specifically about 6000 standard cubic feet per barrel. The temperature of hydrodesulfurization will be chosen from the range of about 600 to 800° F. but in the preferred practice of this invention the temperature will be specifically chosen in the range of 600° to 765° F. Pressures employed in the hydrodesulfurization step will be in the range from about 200 to about 1000 p.s.i.g., and preferably will be between 400 and 800 p.s.i.g.

Considering the data which has been presented, the unique advantages of this invention can be appreciated and the basic nature and advantages of this invention are clearly established. Thus, from the data which have been referred to, when a gas oil is subjected to conventional hydrodesulfurization and then catalytically cracked, 29.1 volume percent of catalytic gasoline is obtainable with 9.4 volume percent of hydrocracked gasoline. However, by using the process of this invention to hydrodesulfurize this gas oil prior to catalytic cracking, while substantially the same amount of total gasoline will be obtained, only about 2.3 volume percent of hydrocracked gasoline will be obtained. It is apparent then that the process of this invention permits the marked increase in the amount of catalytically cracked gasoline obtainable at octane levels above about 90 CFR research. It may also be observed that the process of this invention minimizes the formation of heating oil during the desulfurization operation in a manner contributing to better product distribution of the catalytically cracked gas oil. These and other advantages are achieved while substantially employing the catalytic cracking process because of the higher quality feed stock employed. In this connection, for example, the hydrodesulfurization process of this invention provides a cracking feed stock low in Conradson carbon, reducing the undesired carbonization of the cracking catalyst. Again as indicative of the superiority of this feed stock, the cycle oil obtained in the catalytic cracking operation is of substantially higher value for use in recycle catalytic cracking.

In order to fully indicate the practical application of this invention, reference is made to the accompanying drawing which diagrammatically shows a flow plan embodying the invention.

In this drawing an essentially hydrocarbon feed stock of gas oil boiling range or heavier is first introduced by line 1 to a hydrodesulfurization zone identified by 1a. 75

The feed stock will be desulfurized in zone 1a according to the particular principles referred to hereinbefore.

The hydrodesulfurized products removed from zone 1a through line 2 may be passed to a fractionator 3 permitting segregation of the small percentage of lighter constituents resulting from hydrocracking of the feed stock. Thus, fractionator 3 may be operated to permit removal of the gasoline fraction through line 4 and of a heating oil fraction through line 5. The segregated topped cracking feed stock will then be removed as a bottoms product through line 6 for introduction to catalytic cracking zone 7.

The cracking operation carried out in zone 7 may be of any desired conventional type. Thus, the catalyst may constitute material such as modified natural or synthetic clay or gel type catalysts and particularly active clays, silica-alumina, silica-magnesia compositions or other cracking catalysts. The operation may be of a continuous or batch nature employing fixed beds, moving beds, fluidized or suspensoid systems. The cracking is carried out at temperatures of about 800 to 1000° F. and pressures of about atmospheric to 25 p.s.i.g. or higher.

Cracked products removed from zone 7 through line 8 are fractionated in the product fractionator 9. Fractionator 9 may be operated to permit removal of C₄ and lighter constituents through overhead line 10, gasoline through line 11 and higher boiling fractions through the lower side stream withdrawals 12, 13 and so on and bottom withdrawal 14.

In the practice of this invention the gasoline segregated from line 4 of the process illustrated is obtained in relatively low amounts. This is also true of the heating oil obtained in line 5. The low yield of gasoline and heating oil from this portion of the process is the particular feature of this invention resulting from conduct of the hydrodesulfurization zone in the manner particularly indicated. Because of the extremely small amounts of hydrocracking occurring during hydrodesulfurization it becomes practical to simplify or even eliminate the fractionation requirements of the process. Thus, in this connection fractionator 3 can constitute a simple splitter in which gasoline is removed overhead and heavier products, including heating oil and gas oil, are removed as a bottoms stream. This bottoms stream includes the heating oil of line 5, and the gas oil of line 6 may be passed directly to catalytic cracking zone 7 without necessity for further fractionation. In addition, it is possible to pass products of the hydrodesulfurization zone 1a directly to a catalytic cracking operation without any intermediate fractionation. Inclusion of the hydrocracked gasoline and heating oil in the catalytic cracking zone primarily results in decreasing the capacity of the catalytic cracking zone. While this decrease would be practically intolerable in the case of conventional hydrodesulfurization operation, in the practice of this invention sufficiently small portions of hydrocracked products are formed during hydrodesulfurization so as to make this practicable.

What is claimed is:

1. A process for maximizing the yield of catalytically cracked gasoline of low sulfur content and high octane from a gas oil feed stock and for minimizing the yield of low octane number hydrocracked gasoline which comprises the steps of hydrodesulfurizing a feed stock boiling in the range between about 600° and 1000° F. and comprising a sulfur-containing crude petroleum hydrocarbon in the presence of a catalyst consisting essentially of cobalt molybdate supported on substantially silica-free gamma alumina under hydrodesulfurization conditions including a pressure within the range of about 400 to 800 p.s.i.g., a temperature within the range of about 600° to 765° F., a space velocity within the range of 2 to 4.5 volumes of feed per volume of catalyst per hour and a hydrogen charge rate within the range of 1000 to 6000 cubic feet of hydrogen per barrel of feed stock, said catalyst having been activated at a temperature with-

11

in the range of about 1400° to 1500° F. for a period of about 4 to about 36 hours and having a most frequent pore diameter within the range of about 75 to 200 A., a spread in the more frequent pore diameters within the range of about 10 to 200 A. and a pore distribution factor of more than about 10 and thereafter catalytically cracking at least the gas oil fraction of the products of said hydrodesulfurization reaction to obtain said catalytically cracked gasoline.

2. A process as in claim 1 wherein the said catalyst consists essentially of about 15 weight percent of cobalt molybdate and about 85 weight percent of gamma alumina.

12

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