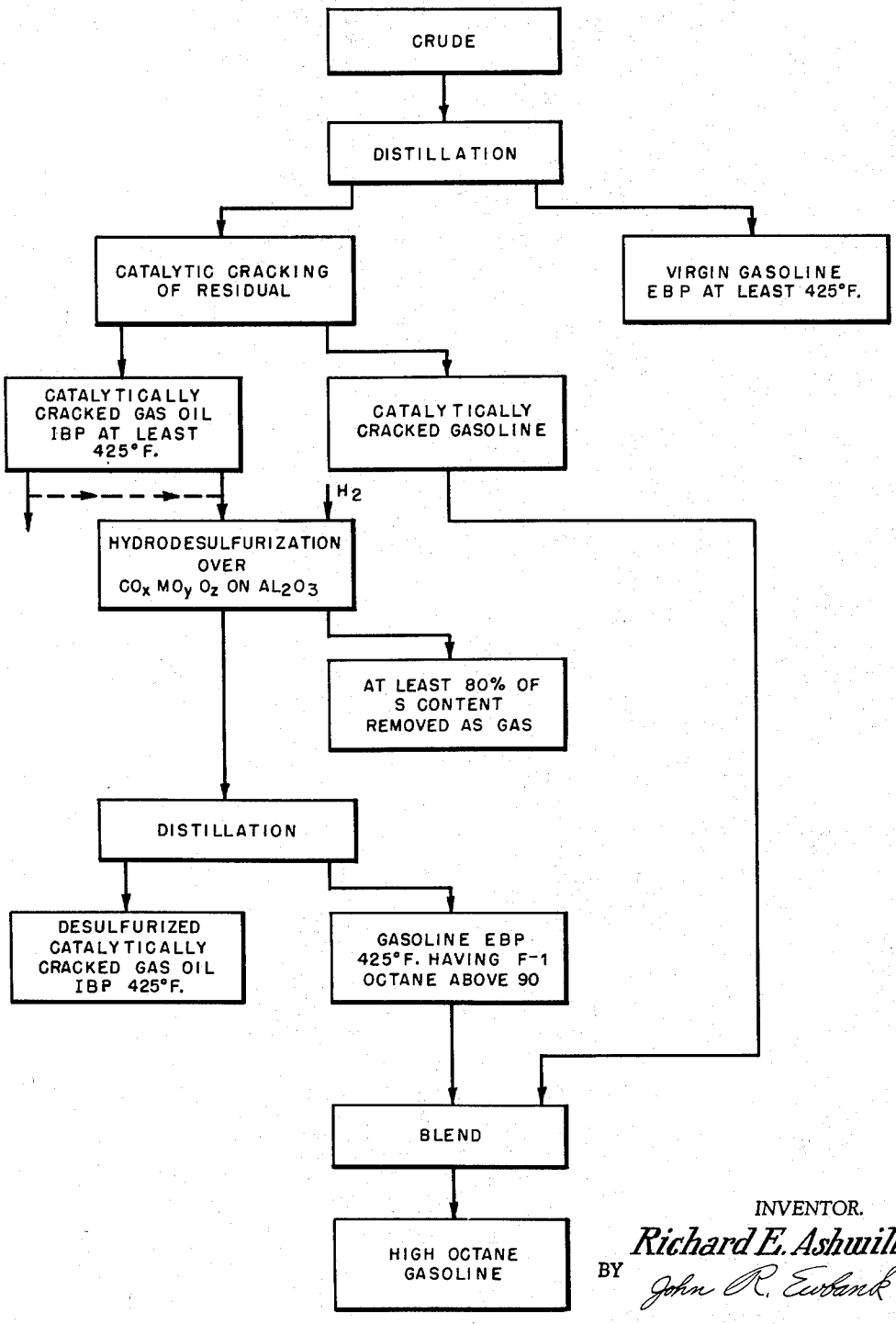
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HYDRODESULFURIZATION OF CATALYTICALLY CRACKED GAS OIL

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HYDRODESULFURIZATION OF CATALYTICALLY CRACKED GAS OIL

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1 Claim. (Cl. 208—93)

This invention relates to the hydrodesulfurization of gas oil.

Heretofore, there have been various proposals relating to the conversion of petroleum products containing troublesome amounts of sulfur. The concentration of sulfur in petroleum products has generally been greater in the less volatile components, thus imposing special sulfur removal problems when dealing with a residual fraction and/or products derived therefrom. The Houdresid method has recently made it possible to catalytically crack the residuum remaining after the removal of at least a portion of the distillable components from a crude petroleum. High octane gasoline is obtained by such catalytic cracking residuum in the presence of significant amounts of steam over a gravitating bed of cracking catalyst. The effluent from the zone in which residuum is catalytically cracked includes the catalytically cracked gasoline and catalytically cracked gas oil (that is, the liquid hydrocarbons boiling above the gasoline boiling range). The catalytically cracked gas oil derived from the catalytic cracking of residuum is sufficiently resistant to further conversions that some effort has been made to utilize all or a part of such catalytic gas oil as fuel oil. Under appropriate conditions, it may be profitable to recycle exhaustively all or a part of the catalytically cracked gas oil derived from the cracking of residuum. An example of a Houdresid method is described in U.S. Patent 2,914,459.

In accordance with the present invention, a crude petroleum is distilled to remove the components boiling below a temperature at least as high as 425° F. and the residuum is catalytically cracked to provide a catalytically cracked gasoline boiling below about 425° F. and a catalytically cracked gas oil derived from residuum and the thus prepared catalytically cracked gas oil is distilled to provide a fraction having a final boiling point below about 650° F. and this light gas oil derived by catalytically cracking residuum is subjected to hydrodesulfurization conditions in the presence of high pressure hydrogen over a catalyst comprising oxides of molybdenum and cobalt on an aluminaceous carrier at conditions sufficiently severe to convert at least four-fifths of the sulfur components in the catalytically cracked gas oil fraction to volatile sulfur compounds such as hydrogen sulfide and to convert a portion of the light gas oild erived by catalytically cracking residuum to components boiling below 425° F. The amount of product boiling below 425° F. is generally within the range from about 2 to about 5 (conveniently expressed as approximately 4) times the sulfur content removed from the light gas oil. That is, for each 1% of sulfur removed from the light gas oil by the hydrodesulfurization, the present invention produces approximately 4% naphtha boiling below 425° F. The components boiling below 425° F. constitute a heavy motor fuel having an F–1 octane number above 90 and consisting predominantly of alkylated benzene hydrocarbons, which heavy motor fuel is especially useful for blending into light motor fuel derived by catalytically cracking residuum.

The flow sheet provides an essentially self-explanatory schematic presentation of the method of the present invention.

The nature of the invention is further clarified by reference to a plurality of sets of experimental data designated as examples.

Example I

A crude petroleum designated as an Eocene-Ratawi crude was distilled to remove all components boiling below about 540 °F., and to provide an 83% residuum. This residuum was catalytically cracked in accordance with the Houdresid method described in U.S. 2,914,459 to provide a high octane catalytically cracked gasoline and a catalytically cracked gas oil suitable for recycling. A 464–627° F. cut of such recycle gas oil had the following characteristics.

Gravity, ° API	21.8
ASTM distillation, ° F.:	
I.B.P.	464
5%	484
10%	490
20%	500
30%	509
40%	518
50%	530
60%	541
70%	556
80%	571
90%	592
95%	606
E.P.	627
Sulfur, wt. percent	3.72
Analysis by silica gel, percent:	
Paraffins plus naphthenes	22.1
Olefins plus aromatics	77.9

This catalytically cracked light gas oil was passed over a catalyst bed of alumina granules impregnated with oxides and/or sulfides of cobalt and molybdenum at a space rate of 2 liquid volumes of gas oil per volume of catalyst per hour at 725° F., 750 p.s.i.g., there being 2000 standard cubic feet of hydrogen per barrel of gas oil. The effluent was cooled condensed, and distilled using a 10 to 1 reflux ratio in a 10 theoretical plate column, and a cut having a 434° F. end point was separated having the following characteristics.

Gravity, ° API	33.0
I.B.P. ° F.	298
5% ° F.	343
10% ° F.	352
20% ° F.	362
30% ° F.	369
40% ° F.	375
50% ° F.	381
60% ° F.	387
70% ° F.	393
80% ° F.	401
90% ° F.	412
95% ° F.	421
E.P. ° F.	434
Analysis by silica gel, percent:	
Paraffins plus naphthenes	18.9
Olefins	1.0
Aromatics	80.1
Octanes:	
W–1 clear	97.6
F–1 plus 3 cc. TEL per gal. (Weise scale)	101.3

This 298–434° F. cut from the effluent from the desulfurization represented 13.8% of the charge to the desulfurization step. Inasmuch as its F–1 clear octane number was 97.6, it was suitable for blending into premium gasoline.

Example II

A residuum from an Eocene-Ratawi crude was catalytically cracked by the method of U.S. 2,914,459. This

provided a 430–650° catalytic gas oil which was 26.4% of the effluent from the cracking zone and 13.4% of the crude. This light gas oil was separated in an 80 plate column at a 3 to 1 reflux ratio and contained 3.57 wt. percent sulfur. It was subjected to hydrodesulfurization at 750° F., 750 p.s.i.g., 2 volume SR and 2000 s.c.f/bbl. of fresh hydrogen over a catalyst consisting predominantly of alumina but containing approximately 18% of oxides of cobalt and molybdenum. The liquid recovery was 96.9 wt. percent and 101 volumes percent of the oil charge. The liquid product was scrubbed with aqueous caustic to remove dissolved hydrogen sulfide, and the liquid contained 0.378% sulfur, indicating about 90% removal of sulfur. Distillation of the desulfurized liquid provided a 280–430° F. cut having an octane number of 94.2 and a volumetric blending octane number of 91.5 when blended with a high sulfur light naphtha (80–200° F.) obtained by cracking a residuum from said Eocene-Ratawi crude. This 280–430° F. cut contained 72.3% aromatics.

Example III

After a virgin gasoline comprising all components boiling below 425° F. is separated from a Mid-Continent crude, the residuum is subjected to the Houdresid cracking process in accordance with U.S. 2,914,459, providing a catalytically cracked gasoline, a light gas oil and a heavy gas oil. The light gas oil is hydrodesulfurized over a catalyst consisting predominantly of sorptive alumina and containing oxides and/or sulfides of cobalt and molybdenum at about 735° F., about 700 pounds per square inch gauge, about 2 liquid volume per volume of catalyst per hour using about 2000 cubic feet of hydrogen per barrel of oil. The 200–430° F. cut from the desulfurized product had a sufficiently high octane number to be useful in premium gasoline.

Obviously many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claim.

What is claimed is:

In a method in which a crude petroleum is fractionated to remove components boiling below a temperature at least as high as 425° F. and the residual hydrocarbonaceous materials are catalytically cracked to form fractions comprising catalytically cracked gasoline and catalytically cracked liquid hydrocarbonaceous materials free from components boiling in the gasoline range, the improvement which comprises the steps of: subjecting a fraction boiling within the range from about 425 to about 650° F. of said catalytically cracked liquid hydrocarbonaceous material to catalytic hydrodesulfurization at an elevated temperature of about 750° F. and at about 750 p.s.i.g. pressure over a catalyst comprising oxides of molybdeum and cobalt on an alumina carrier at a space rate of about 2 volumes of liquid per volume of catalyst per hour in the presence of about 2000 cubic feet of hydrogen per barrel of hydrocarbon to convert at least four-fifths of the sulfur components in the catalytically cracked liquid hydrocarbonaceous material to volatile sulfur compounds and to form some normally liquid hydrocarbons boiling below 425° F.; separating as a valuable product of the hydrodesulfurization a liquid hydrocarbon having an F–1 octane number above 90 by fractionally distilling a fraction consisting essentially of hydrocarbons boiling entirely below 425° F., from the normally liquid effluent from such hydrodesulfurization; and withdrawing such fraction and blending it into the catalytically cracked gasoline to provide a high octane gasoline.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,115,455 December 24, 1963

Richard E. Ashwill

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

Column 1, line 54, for "oild erived" read -- oil derived --; column 2, line 62, for "W-1" read -- F-1 --; column 4, line 13, for "molybdeum" read -- molybdenum --.

Signed and sealed this 7th day of July 1964.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents