

[54] **INTEGRATED HYDROCARBON
CONVERSION PROCESS**

[75] Inventor: **John E. Walkey**, Richmond, Calif.

[73] Assignee: **Chevron Research Company**, San Francisco, Calif.

[22] Filed: **June 21, 1973**

[21] Appl. No.: **372,117**

[52] U.S. Cl. **208/50; 208/58; 208/89;**

208/93

[51] Int. Cl. **C10g 37/06**

[58] Field of Search **208/58, 89, 93, 50**

[56] **References Cited**

UNITED STATES PATENTS

2,871,182	1/1959	Weekman	208/50
3,493,489	2/1970	Naniche	208/50
3,617,501	11/1971	Eng et al.	208/97
3,684,688	8/1972	Roselius	208/50
3,704,224	11/1972	Scovill et al.	208/50
3,775,290	11/1973	Peterson et al.	208/89

Primary Examiner—Herbert Levine

Attorney, Agent, or Firm—G. F. Magdeburger; R. H. Davies

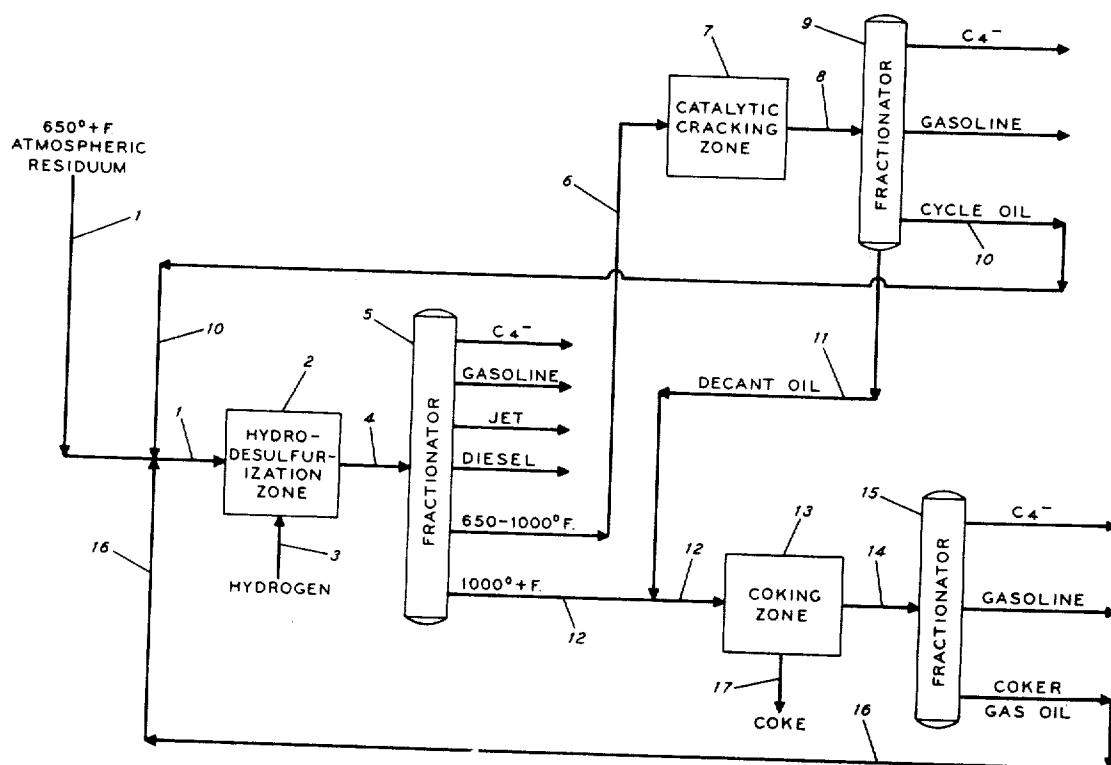
[57]

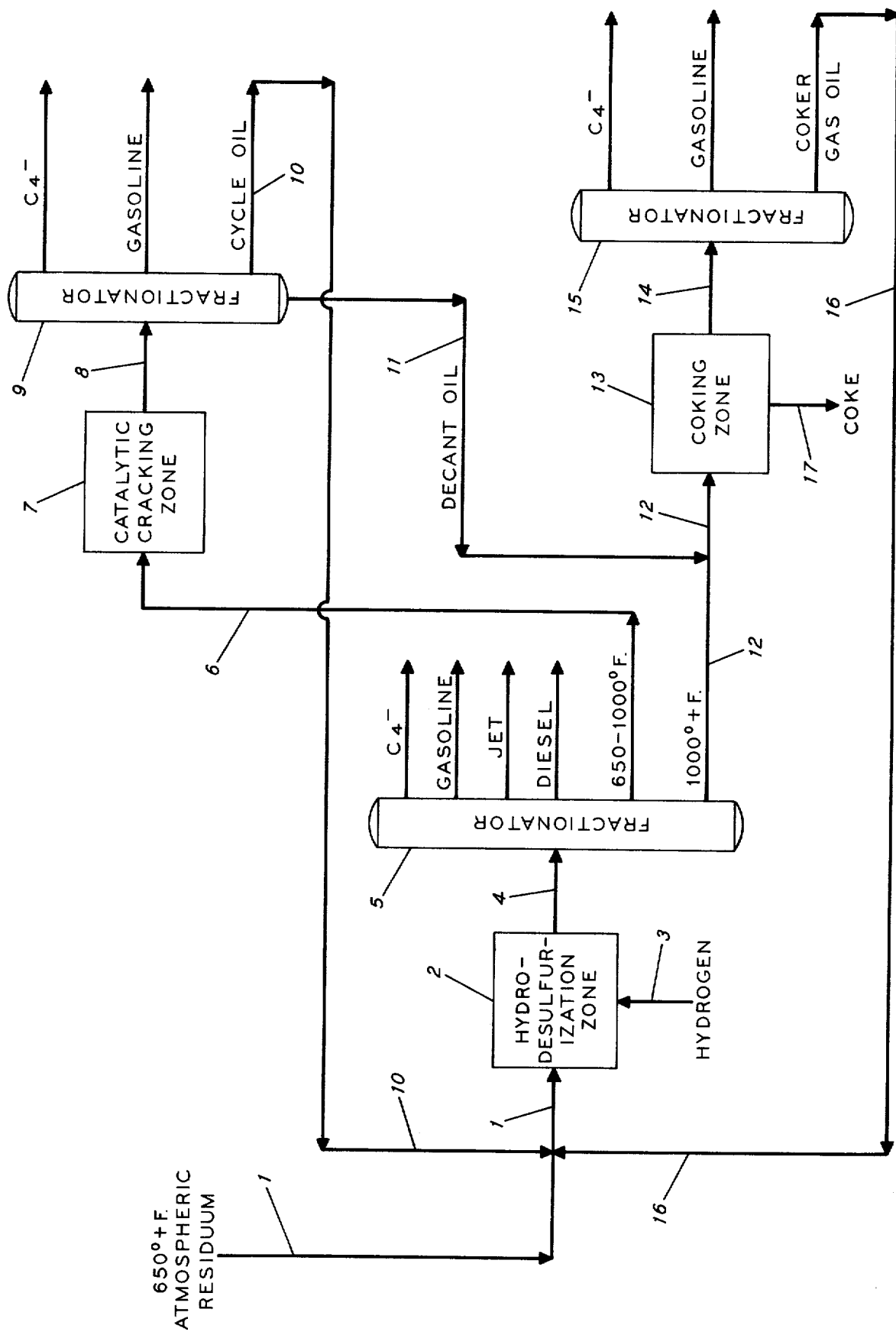
ABSTRACT

An integrated hydrocarbon conversion process for converting a heavy hydrocarbon feedstock boiling above 650°F. into various valuable products including gasoline, jet fuel, and coke, which comprises:

- hydrodesulfurizing the feedstock in a hydrodesulfurization zone;
- catalytically cracking at least a portion of the fraction from the hydrodesulfurization zone boiling in the range of about 650° to about 1000°F.;
- feeding at least a portion of the decant oil from the catalytic cracking zone and at least a portion of the fraction from the hydrodesulfurization zone boiling above about 1,000°F. to a coking zone and coking the mixture;
- recycling at least a portion of the catalytic cracker cycle oil and the coker gas oil to the hydrodesulfurization zone; and
- recovering as products of the integrated hydrocarbon conversion process at least gasoline, jet fuel, and coke.

2 Claims, 1 Drawing Figure





INTEGRATED HYDROCARBON CONVERSION PROCESS

BACKGROUND OF THE INVENTION

A continuously rising demand for crude oil combined with a shrinking supply has created what is now being referred to in the United States as an energy crisis. In view of these conflicting developments, it is incumbent upon refiners to squeeze every last possible drop of useful product out of each barrel of crude oil. The combination of processes for the refining of heavy hydrocarbon feedstocks boiling above 650°F. which will optimize the yields and selectivity of the products obtained is particularly desirable since these feedstocks, e.g., atmospheric residuum, are generally of low value and difficult to process.

The subject invention is directed to the combination of three processes in a unique manner which concurrently improves (1) product yields and product qualities from the combined processes while (2) improving the efficiency of all three processes.

SUMMARY OF THE INVENTION

An integrated hydrocarbon conversion process for converting a heavy hydrocarbon feedstock boiling above 650°F. into various valuable products including gasoline, jet fuel, and coke, which comprises:

- a. hydrodesulfurizing the feedstock in a hydrodesulfurization zone thereby obtaining an effluent comprising gasoline, jet fuel, a fraction comprising material boiling in the range of from about 650° to about 1000°F., and a fraction comprising material boiling above about 1000°F.;
- b. catalytically cracking at least a portion of the fraction from the hydrodesulfurization zone boiling in the range of about 650° to about 1000°F., thereby obtaining an effluent comprising gasoline, catalytic cracker cycle oil, and a decant oil;
- c. feeding at least a portion of the decant oil and at least a portion of the fraction from the hydrodesulfurization zone boiling above about 1000°F. to a coking zone and coking the decant oil and the fraction boiling above about 1000°F., thereby obtaining an effluent comprising gasoline, coker gas oil and coke;
- d. recycling at least a portion of the catalytic cracker cycle oil and the coker gas oil to the hydrodesulfurization zone and hydroconverting the catalytic cracker cycle oil and coker gas oil therein; and
- e. recovering as products of the integrated hydrocarbon conversion process at least gasoline, jet fuel, and coke.

BRIEF DESCRIPTION OF THE DRAWING

The drawing is a schematic flow diagram of one embodiment of the process.

DETAILED DESCRIPTION OF THE INVENTION

The subject invention is directed to an integrated hydrocarbon conversion process for converting heavy hydrocarbon feedstocks boiling above 650°F. and containing substantial quantities of materials boiling above 1000°F. into various valuable products in good yield and with good selectivity for producing the more valuable products. The process of the subject invention utilizes a hydrodesulfurization zone, a catalytic cracking zone, and a coker, in a particular mode of operation

which optimizes the operating efficiency of all three units.

The method of operation has been summarized above under "SUMMARY OF THE INVENTION." It will be described in more detail hereinafter. Basically it calls for an integrated process combining hydrodesulfurization, catalytic cracking and coking. Products recovered using the integrated process of this invention include at least gasoline, jet fuel and coke.

Additionally, diesel fuel may be recovered as well as middle distillates for use as fuel oil. Light gases are also produced which may be handled by conventional means and used for conventional purposes.

HEAVY HYDROCARBON FEEDSTOCKS

The heavy hydrocarbon feedstocks utilized in the subject invention comprise hydrocarbons boiling above about 650°F. and contain substantial quantities of material boiling above 1000°F. A typical feedstock is that normally produced as the residuum product from atmospheric-pressure distillation of crude oil. The initial boiling point of the feedstock can be as low as about 350°F. if it is desired to hydrodesulfurize the 350° to 650°F. boiling range fraction in the crude oil. Other feedstocks include heavy hydrocarbons recovered from tar sands, synthetic crude oil recovered from oil shales, heavy oils produced from liquefaction of coal, etc. The hydrocarbon feedstocks will generally contain at least about 10 percent of materials boiling above 1000°F.

OPERATING CONDITIONS IN THE HYDRODESULFURIZATION ZONE

Hydrodesulfurization of the heavy hydrocarbon feedstock is carried out at conventional operating conditions which will generally include a temperature in the range of about 650° to about 850°F., preferably within the range of from about 700° to about 800°F., a liquid hourly space velocity of from about 0.1 to about 3, preferably about 0.3 to about 1.5, and a pressure of from about 500 to about 3,000 psig, preferably about 1,000 to about 2,000 psig.

The hydrogen supply rate (makeup and recycle hydrogen) to the hydrodesulfurization zone will generally be in the range of from about 500 to 20,000 SCF/barrel, preferably in the range from about 1,000 to about 10,000 SCF/barrel of feed, and more preferably in the range of from about 2,000 to about 4,000 SCF/barrel.

While hydrodesulfurization of the hydrocarbon feedstock fed to the hydrodesulfurization zone is the primary purpose of this zone, other reactions encompassed within the term hydroconversion, e.g., hydrogenation and hydrodenitrification, may be occurring.

HYDRODESULFURIZATION CATALYST

The hydrodesulfurization catalyst utilized in the subject invention can comprise any conventional hydrodesulfurization catalyst. Normally these catalysts comprise composites comprising at least one hydrogenating component selected from Group VI metals and compounds of Group VI metals and at least one hydrogenating component selected from Group VIII metals and compounds of Group VIII metals together with a refractory support such as alumina, silica-alumina, silica-alumina-titania, and combinations of amorphous inorganic oxides with a zeolite.

A preferred hydrodesulfurization catalyst comprises a carrier of alumina in which discrete, substantially insoluble metal phosphate particles are dispersed in said carrier and consisting essentially of at least one metal phosphate selected from phosphates of the zirconium, titanium, tin, thorium, cerium and hafnium, and containing substantially the entire phosphorus content of the said catalyst. Preferred insoluble metal phosphate components are phosphates of zirconium and titanium.

The general type of insoluble metal phosphate containing catalyst and procedure for making this catalyst is disclosed in U.S. Pat. Nos. 3,546,105 and 3,493,517, both of which patents are incorporated herein by reference. As in U.S. Pat. No. 3,546,105, substantially no silica or potentially deleterious fluorine are present in these preferred catalysts.

OPERATING CONDITIONS IN THE CATALYTIC CRACKING ZONE

Operating conditions utilized in the catalytic cracking zone of the subject invention are those conventional in catalytic cracking of hydrocarbon feedstocks. These generally include a temperature in the range of from about 850° to about 1100°F., a pressure in the range of from about 1 to about 100 psig, preferably 5 to 30 psig. The liquid hourly space velocities within the catalytic cracking zone will generally fall within the range of from about 1.5 to about 50, although space velocities as high as 100 or more in riser cracking units may be used. Preferred temperatures for use in the catalytic cracking zone will generally fall within the range of from about 850° to about 1050°F.

The catalytic cracking process step including regeneration of the catalyst may be performed utilizing well-known techniques, including, for example, fluidized bed or moving bed processes.

CATALYTIC CRACKING CATALYSTS

The catalysts used in the catalytic cracking zone in the process of the present invention are those conventionally utilized in catalytic cracking processes. For example, activated, naturally occurring catalytic cracking catalysts such as clay, i.e., kaolin, can be used, as well as synthetic clays such as those disclosed in U.S. Pat. No. 3,252,889, and semi-synthetic catalysts such as silica-alumina to which kaolin has been added. Synthetically prepared cracking catalysts containing amorphous silica-alumina, with or without additional promoters, can also be used. Zeolite-containing catalysts may also be used to reduce coke formation. Methods of preparation of the amorphous catalytic cracking catalysts are well known. The crystalline zeolitic aluminosilicate catalysts are disclosed and discussed in great detail in U.S. Pat. Nos. 3,210,267 and 3,271,418. As is disclosed in these two prior art patents, the crystalline zeolitic molecular sieve component may have included therewith an amorphous matrix, for example, silica-alumina, titania, zirconia, magnesia, and the like.

It should be recognized that different hydrocarbon feeds present different problems and the catalyst used will, in general, be tailored to fit the particular needs of the hydrocarbon feedstock being used.

OPERATING CONDITIONS IN THE COKING ZONE

The coking zone in the subject invention utilizes conventional operating techniques and conditions. Typically, it may comprise either one of two different types

of coking steps; namely, delayed coking or fluid coking. These are described in detail in U.S. Pat. No. 3,493,489, the disclosure of which is hereby incorporated by reference. Additional patents including U.S. Pat. Nos. 3,537,975 and 3,518,182 discuss fluid coking and delayed coking, respectively.

DEFINITIONS OF TERMS

The term "decant oil," as used herein, means the heavy bottoms fraction of the effluent from the catalytic cracking zone. Typically it will boil in the range 800° to about 1000°F.

The catalytic cracking cycle oil which is recycled (at least in part) to the hydrodesulfurization may encompass both the light cycle oil typically boiling in the range 430° to 650°F., and the heavy cycle oil typically boiling in the range 650° to 800°F. Part of this catalytic cracker cycle oil may also be recovered for use as fuel oil.

The "coker gas oil" referred to herein typically boils in the range of 400° to 900°F.

The term "C₄-'' means hydrocarbons having 4 or less carbon atoms. "C₄-'' hydrocarbons recovered in fractionator 5 will be saturated. Off of fractionator 9, the "C₄-'' hydrocarbon fraction will contain unsaturated hydrocarbons. Similarly, the C₄- hydrocarbon fraction from fractionator 15 may also contain unsaturated compounds.

PROCESS OPERATION

Referring now to the drawing which represents a preferred embodiment of the present invention, an atmospheric residuum boiling above 650°F. is fed by line 1 to hydrodesulfurization zone 2. Hydrogen is introduced into hydrodesulfurization zone 2 via line 3. The effluent from hydrodesulfurization zone 2 is fed by line 4 to fractionator 5 where various cuts are taken off as noted in the drawing. This fractionator may consist of two stages, i.e., an atmospheric column and a vacuum column. A fraction comprising hydrocarbons boiling in the range of from 650° to 1000°F. is fed by line 6 to catalytic cracking zone 7. The effluent from catalytic cracking zone 7 is fed by line 8 to fractionator 9 wherein various cuts are obtained, as indicated in the drawing. A catalytic cracking cycle oil which comprises material boiling in the range of 430° to 800°F. is removed by line 10 and recycled to hydrodesulfurization zone 2. A decant oil comprising material boiling above about 800°F. and primarily in the range of 800° to 1000°F. is removed by line 11 and sent by lines 11 and 12 to coking zone 13. Additional feed to coking zone 13 comprises the material boiling above 1000°F. from hydrodesulfurization zone 2. This material is fed to coking zone 13 by line 12. The effluent from coking zone 13 is sent by line 14 to a fractionator 15 wherein various cuts are removed as noted in the drawing. A coker gas oil is recycled by line 16 to hydrodesulfurization zone 2. Coke is removed by line 17.

By the process described in the figure, liquid products, including gasoline, jet fuel, diesel fuel as desired, and coke are obtained in good yield and with high selectivity for the most desirable products, e.g., gasoline and jet fuel.

As is evident from the drawing, the feed to the catalytic cracking zone is desulfurized and hydrogenated in hydrodesulfurization zone 2. Rather than recycling the catalytic cracking zone cycle oil to the catalytic crack-

5

ing zone as is conventionally done, the catalytic cracking cycle oil is recycled to the hydrosulfurization zone to improve its quality as a product and as feedstock to the catalytic cracking zone.

Rather than feeding coker gas oil to the catalytic cracking zone as is conventionally done, it is recycled to the hydrosulfurization zone for hydrogenation to improve its quality as a catalytic cracking zone feed. Middle distillate boiling range products derived from catalytic cracking and coking are then hydrogenated in the hydrosulfurization zone and can be drawn off as product from fractionator 5 as desired.

The benefits derived from this process and combination are derived in part from the introduction of distillate stocks, i.e., a catalytic cracking zone cycle oil and coker gas oil, into the hydrosulfurization zone together with the hydrocarbon feedstock. From the standpoint of operating efficiency, this is more effective than utilizing separate hydrosulfurization zones for these materials. Additionally, improved desulfurization can be obtained by combining lower boiling components, i.e., cycle oil from the catalytic cracking zone and coker gas oil with the heavy hydrocarbon feedstock to a desulfurization zone. Further, hydrosulfurization of the coker feed improves the yields and the quality of products from the coking zone. Similarly, the hydrogenation of coker gas oil before feeding it to a catalytic cracking zone improves its quality as catalytic cracking zone feed. Similarly, hydrogenation of the 650° to 1000°F. boiling range stock in the heavy hydrocarbon feed improves its quality as catalytic cracking zone feed.

In summary, the unique integrated combination of processing steps of the subject invention provide improved feedstocks to each of the three processing zones. Improved operating efficiency results together with improved yields of high quality products.

It is apparent that many widely differing embodiments of this invention may be made without departing from the scope and spirit thereof; and, therefore, it is not intended to be limited except as indicated in the appended claims.

What is claimed is:

1. In a process wherein an atmospheric residuum hy-

6

drocarbon stock containing sulfur and substantial quantities of materials boiling above 1000°F. is hydrotreated in a hydrotreating zone, a low sulfur gasoline product and a low sulfur jet fuel product are recovered from the effluent from said hydrotreating zone, a low sulfur portion of said effluent is catalytically cracked in a catalytic cracking zone; at least a portion of said effluent boiling above 1000°F. is coked in a coking zone, a gasoline product is recovered from the effluent from said catalytic cracking zone, a portion of the effluent from said catalytic cracking zone is recycled to said hydrotreating zone, and a gasoline product is recovered from the effluent from said coking zone, the improved method of optimizing the operating efficiency of the combination of said hydrotreating, catalytic cracking and coking zones which comprises:

- 1 limiting to 800°F. the end point of said portion of said effluent from said catalytic cracking zone that is recycled to said hydrotreating zone;
- 2 passing to said coking zone and coking the portion of said effluent from said catalytic cracking zone that boils above 800°F.;
- 3 recovering coke from said coking zone in increased yield compared with the yield if the portion of said effluent from said catalytic cracking zone boiling above 800°F. were not coked in said coking zone;
- 4 recycling from said coking zone to said hydrotreating zone a coker gas oil in increased amount compared with the amount available for such recycle if the portion of said effluent from said catalytic cracking zone boiling above 800°F. were not coked in said coking zone;

whereby there is obtained increased coke yield, increased coker gas oil for recycle to said hydrotreating zone, and improved desulfurization efficiency in said hydrotreating zone, with a resulting increased efficiency of operation of the combination of said hydrotreating, catalytic cracking and coking zones.

2. A process as in claim 1 wherein the catalyst in said hydrotreating zone comprises a Group VI-B component, a Group VIII component, a refractory component and insoluble metal phosphate particles dispersed through said refractory component.

* * * * *

45

50

55

60

65