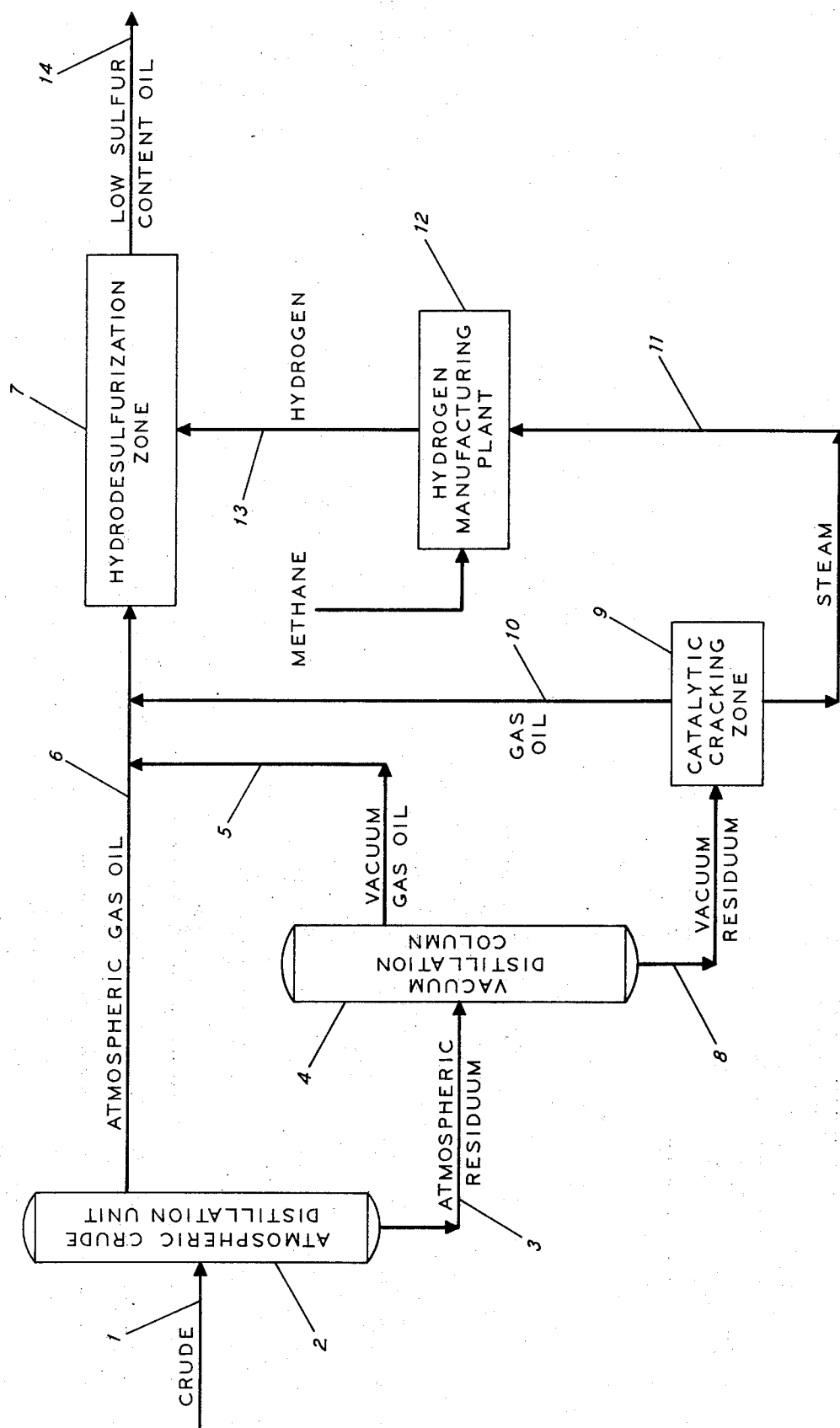


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INTEGRATED PROCESS COMBINING CATALYST CRACKING
WITH HYDROTREATING
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**INTEGRATED PROCESS COMBINING CATALYTIC
CRACKING WITH HYDROTREATING**
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6 Claims

ABSTRACT OF THE DISCLOSURE

An integrated process is disclosed, comprising catalytically cracking a hydrocarbon feedstock in a catalytic cracking zone; passing the gas oil portion of the effluent from the catalytic cracking zone to a hydrotreating zone; regenerating the catalytic cracking catalyst used in the catalytic cracking zone by burning carbonaceous deposits therefrom, thereby producing heat; heating water to produce steam using this heat; producing hydrogen from this steam; passing at least a portion of the hydrogen formed to the hydrotreating zone; and catalytically hydrotreating the gas oil portion in the hydrotreating zone. Alternatively, the hydrogen can be produced by reacting the carbonaceous deposits on the catalytic cracking catalyst with steam.

BACKGROUND OF THE INVENTION

Field

With the growing demand for improved air quality, a need for the desulfurization of fuel oils, diesel oils, and the like, to lower and lower levels of sulfur content is a foregone conclusion. Many major cities in the United States presently have sulfur content level requirements for fuel oil of 0.5% by weight. It is contemplated that even lower levels, on the order of 0.3% or even less, are in the not-too-distant future.

In view of the continuing and increasing demand for low-sulfur-content hydrocarbon oils, the development of efficient methods for reducing the sulfur content of heavy hydrocracking feedstocks is of continuing and increasing concern. This invention is directed to a process for preparing valuable hydrocarbon products from liquid hydrocarbon streams, particularly heavy hydrocarbon streams, and particularly for the production of low-sulfur-level fuel oil from residual stocks after distillation of crude oil. By the process of this invention, effective use is made of the heat produced in the catalytic cracker regenerator to provide hydrogen for the hydrotreating process step.

Prior art

Removal of sulfur from hydrocarbon feedstocks is well known. Numerous patents have issued directed to such processes. Additionally, catalytic cracking of heavy hydrocarbon feedstocks is also well known.

U.S. Pat. 3,185,639 teaches distilling a crude oil, deasphalting the residuum, sending the deasphalted residuum to a catalytic cracking zone, and sending the cycle oil which constitutes part of the effluent from the catalytic cracker to a hydrofining zone and subsequently to a hydrocracking zone.

U.S. Pat. 3,193,488 teaches distilling a crude oil and sending the topped crude to a catalytic cracker. A portion of the cycle oil constituting a portion of the effluent from the catalytic cracker is solvent extracted and sent to a hydrocracking zone.

U.S. Pat. 2,880,167 teaches catalytic cracking of heavy-low-boiling petroleum oils containing nonvaporizable constituents at ordinary pressures with the temperature in the cracking zone being maintained to form heavy distillate fuels or gasoline.

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U.S. Pat. 2,994,659 teaches catalytic cracking of residual oils, topped crude and reduced crudes, burning the carbon off the catalyst to form steam (heat exchange) and operation of the catalytic cracker at a wide variety of conditions, dependent on the conversion desired.

U.S. Pat. 2,919,244 teaches using a heavy gas oil effluent of a catalytic cracker which is normally recycled for the generation of steam if a power failure occurs.

U.S. Pat. 2,662,050 teaches catalytic cracking of reduced crude to gasoline with minor quantities of a heavy gas oil, a No. 5 fuel oil and a No. 3 heating oil also produced.

U.S. Pat. 3,008,896 teaches catalytic cracking of residual oils or topped crudes at low (30%) conversion to light distillates and higher (70%) conversion to cycle gas oils, which are then recovered and processed in a gas oil catalytic cracking system.

In an article in "Chemical & Engineering News," 50#14:15 (4/3/72), and also in "Oil & Gas Journal," 70#14:30 (4/3/72), a process is described for producing high-octane gasoline by fluid catalytic cracking directly from the residual fractions remaining after crude oil is fractionated. Zeolite catalysts and steam generation during coke burnoff in the catalyst regenerator are taught.

SUMMARY OF THE INVENTION

An integrated process is disclosed, comprising:

(A) catalytically cracking a hydrocarbon feedstock in a catalytic cracking zone;

(B) passing the gas oil portion of the effluent from the catalytic cracking zone to a hydrotreating zone;

(C) regenerating the catalytic cracking catalyst used in the catalytic cracking zone by burning carbonaceous deposits therefrom, thereby producing heat;

(D) heating water to produce steam using this heat;

(E) passing the hydrogen formed to the hydrotreating zone; and

(F) catalytically hydrotreating said gas oil portion in said hydrotreating zone.

Alternatively, the carbonaceous deposits can be reacted with water to directly produce hydrogen, which is then used in the hydrotreating zone.

The process of the present invention is particularly useful with heavy hydrocarbon feedstocks such as reduced topped crude oils, atmospheric residua, crude shale oils, coal tar distillates, and the like. Mixtures of crude oils and distillate fractions as well as mixtures of petroleum crudes and crude shale oils, etc., are also satisfactory feedstocks.

The hydrogen formed from the steam generated from burning the carbonaceous deposits on the catalytic cracking catalyst is preferably formed by steam reforming methane, LPG or naphtha.

DETAILED DESCRIPTION OF THE INVENTION

Drawing

The drawing (FIG. 1) is a diagrammatic illustration of apparatus and flow paths suitable for carrying out one embodiment of the process of the present invention.

Statement of the invention

In accordance with the present invention, there is provided a process which comprises catalytically cracking a hydrocarbon feedstock in a catalytic cracking zone, passing the gas oil portion of the effluent from the catalytic cracking zone to a hydrotreating zone, regenerating the catalytic cracking catalyst used in the catalytic cracking zone by burning carbonaceous deposits therefrom with a net production of heat, heating water to produce steam using this heat, producing hydrogen from the steam, passing at least a portion of the hydrogen

to the hydrotreating zone, and catalytically hydrotreating the gas oil portion.

Operating conditions in catalytic cracking zone

The catalytic cracking zone will be operated at a temperature of from 875° to 1025° F., preferably 925° to 975° F., at a pressure from 1 to 100 p.s.i.g., preferably 10 to 30 p.s.i.g., more preferably 15 to 20 p.s.i.g., a liquid hourly space velocity of from 0.5 to 100 or higher, and a conversion rate of from 40% to 85%.

The catalytic cracking zone is preferably operated to produce a major proportion of gas oil, i.e., greater than 50% (liquid volume) of the effluent from the catalytic cracking zone will boil in the gas oil range of from about 400° to about 1000° F.

Hydrocarbon feedstocks

While any hydrocarbon feedstock that is suitable for feeding to a catalytic cracking zone can be used in the process of the present invention, substantial quantities of gas oil must be recoverable from the effluent from the catalytic cracking zone. Hence, heavy hydrocarbon feedstocks such as reduced topped crude oils, atmospheric residual, crude shale oils, coal tar distillates, and the like, are particularly preferred. Mixtures of crude oils and distillate fractions as well as mixtures of petroleum crudes and crude shale oils, etc., are also satisfactory feedstocks. The feedstocks used preferably contain substantial quantities of materials boiling about 1000° F.

The yield of gas oil can be maximized by using a once-through operation and keeping conversion rates low. If higher yields of the lower-boiling gas oils are desired (e.g., No. 2 oil in the 400°–650° F. range), lower temperatures and recycle can be utilized.

Catalytic cracking catalyst

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. 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 amorphous catalytic cracking catalysts are well known. The crystalline zeolitic molecular sieve catalysts are disclosed and discussed in great detail in U.S. Pats. 3,210,267 and 3,271,418.

It should be recognized that different hydrocarbon feeds to the catalytic cracker 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 hydrotreating zone

The term "hydrotreating" as used herein is meant to encompass both hydrofining (i.e., hydrosulfurization and hydrodenitrification) and hydrocracking.

The hydrotreating is carried out at a temperature of from about 500° to 850° F., preferably 700° to 800° F., a pressure of from 200 to 10,000 p.s.i.g., preferably about 500 to about 1500 p.s.i.g., and at a liquid hourly space velocity of from 0.2 to 10.0, preferably 2.0 to 5.0. The hydrogen supply rate (makeup and recycle hydrogen) to the hydrotreating zone is in the range of from about 1000 to about 10,000 s.c.f./bbl., preferably about 2000 to about 5000 s.c.f./bbl. The preferred conditions specified herein refer to hydrofining operation of the hydrotreating zone. The operating temperature during the onstream period is preferably maintained at as low a value as possible, consistent with maintaining adequate desulfurization of the hydrotreating zone feedstock. It should be noted that while hydrosulfurization will generally be the primary concern in the hydrotreating

zone, denitrification and hydrocracking may also be of importance, dependent upon (1) the hydrocarbon feedstock, and (2) the desired products, respectively.

Hydrotreating catalyst

The catalyst employed in the hydrotreating zone comprises a material having hydrogenation-dehydrogenation activity together with an active cracking component. Exemplary cracking components include silica-alumina, silica-magnesia, silica-alumina-zirconia composites, acid-treated clays, and similar materials. The hydrogenation-dehydrogenation components of the catalyst comprise at least one hydrogenation component selected from Group VI metals and compounds of Group VI metals and at least one hydrogenation component selected from Group VIII metals and compounds of Group VIII metals. Preferred combinations of hydrogenation components include nickel sulfide with molybdenum sulfide, cobalt sulfide with molybdenum sulfide, cobalt with molybdenum, and nickel with tungsten.

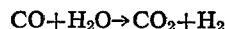
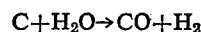
The preferred hydrotreating catalyst comprises a carrier of alumina together with hydrogenation components from Group VI and Group VIII metals and compounds thereof and in which discrete, substantially insoluble metal phosphate particles are dispersed and containing at least one metal phosphate selected from phosphates of zirconium, titanium, tin, thorium, cerium and hafnium, and containing substantially the entire phosphorus content of the catalyst. Preferred insoluble metal phosphate components are phosphates of zirconium and titanium.

This general type of catalyst and the procedure for making it are disclosed in U.S. Pats. 3,546,105 and 3,493,517, both of which patents are incorporated herein by reference.

Hydrogen manufacture

Processes for manufacturing hydrogen from steam are well known. See, for example, volume 7 of the Encyclopedia of Chemical Technology (1951), pp. 679–681).

The preferred method in the process of the present invention is to steam reform methane, LPG, or naphtha. Alternatively, the carbonaceous deposits on the catalytic cracking catalyst can be utilized directly to form H₂ by the water-gas reaction



This operation can be carried out in a fluidized bed or the like.

Process operation

Referring now to FIG. 1, which represents a preferred embodiment of the present invention, a hydrocarbon feedstock comprised of a crude oil is fed via line 1 to atmospheric crude distillation unit 2. Atmospheric residuum is removed via line 3 and sent to vacuum distillation column 4. A vacuum gas oil fraction is taken off via line 5 and combined with an atmospheric gas oil and fed via line 6 to hydrosulfurization zone 7. The vacuum residuum from vacuum distillation column 4 is fed via line 8 to catalytic cracking zone 9. The gas oil produced in catalytic cracking zone 9 is fed via line 10 and line 6 to hydrosulfurization zone 7. The steam generated in catalytic cracking zone 9 is fed via line 11 to hydrogen manufacturing plant 12. Hydrogen formed in plant 12 is then fed to hydrosulfurization zone 7 via line 13. A low-sulfur-content fuel oil is removed from hydrosulfurization zone 7 via line 14.

While the drawing constitutes one preferred embodiment of the present invention, it is clear that various modifications can be made in the present invention without departing from the spirit thereof. For instance, the gas oil from the catalytic cracking zone need not be combined with the atmospheric gas oil and vacuum gas oil.

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It can serve as the sole feedstock to a hydrofining zone. Similarly, it may simply be combined with the vacuum gas oil and fed to a hydrofining zone. Additionally, as previously pointed out, a wide variety of hydrocarbon feedstocks may be utilized. Preferably, the heavy hydrocarbon feedstocks to the catalytic cracking zone contain substantial amounts of material boiling above 1000° F.

What is claimed is:

1. An integrated process which comprises:

(A) catalytically cracking a hydrocarbon feedstock in a catalytic cracking zone;

(B) passing the gas oil portion of the effluent from said catalytic cracking zone to a hydrotreating zone;

(C) regenerating the catalytic cracking catalyst used in said catalytic cracking zone by burning carbonaceous deposits therefrom, with a net production of heat;

(D) heating water to produce steam, using the heat generated in step C;

(E) producing hydrogen from said steam;

(F) passing at least a portion of said hydrogen to said hydrotreating zone; and

(G) catalytically hydrotreating said gas oil portion in said hydrotreating zone.

2. The process of claim 1, wherein said hydrocarbon stock contains substantial amounts of materials boiling above 1000° F.

3. The process of claim 2, wherein said hydrocarbon stock is a vacuum residuum.

4. The process of claim 1, wherein said steam is converted to hydrogen by steam reforming methane, LPG or naphtha.

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5. The process of claim 1, wherein said catalytic cracking zone is operated to produce as the major product, on a volume basis, said gas oil portion.

6. The process of claim 1, wherein said catalytic cracking zone is operated at a temperature from 875° to 1025° F., a pressure from 1 to 100 p.s.i.g., a liquid hourly space velocity from 0.5 to 100; said hydrotreating zone is operated at a pressure of from 200 to 10,000 p.s.i.g., a temperature from 500° to 850° F., a liquid hourly space velocity of from 0.2 to 10.0, and a hydrogen supply rate of 500 to 20,000 s.c.f./barrel of feed to said hydrotreating zone.

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