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[21] Appl. No. 757,939
[22] Filed Sept. 6, 1968
[45] Patented Nov. 2, 1971
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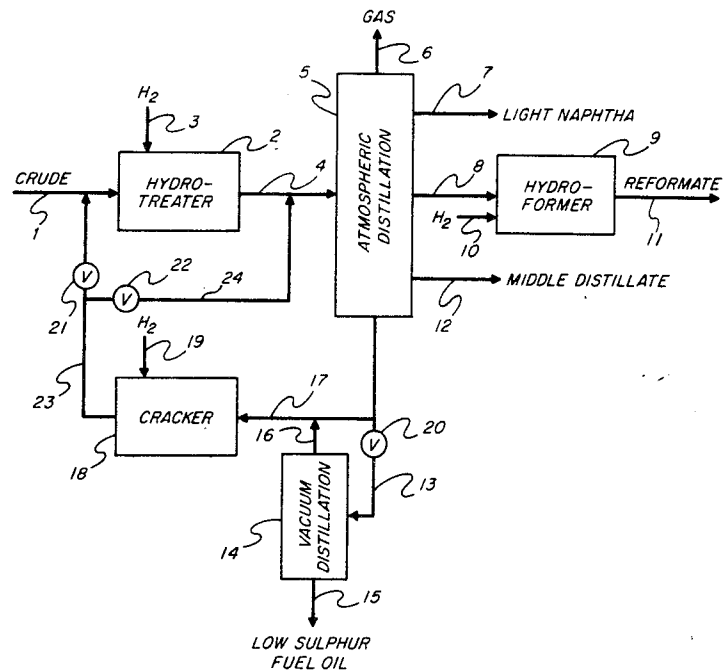
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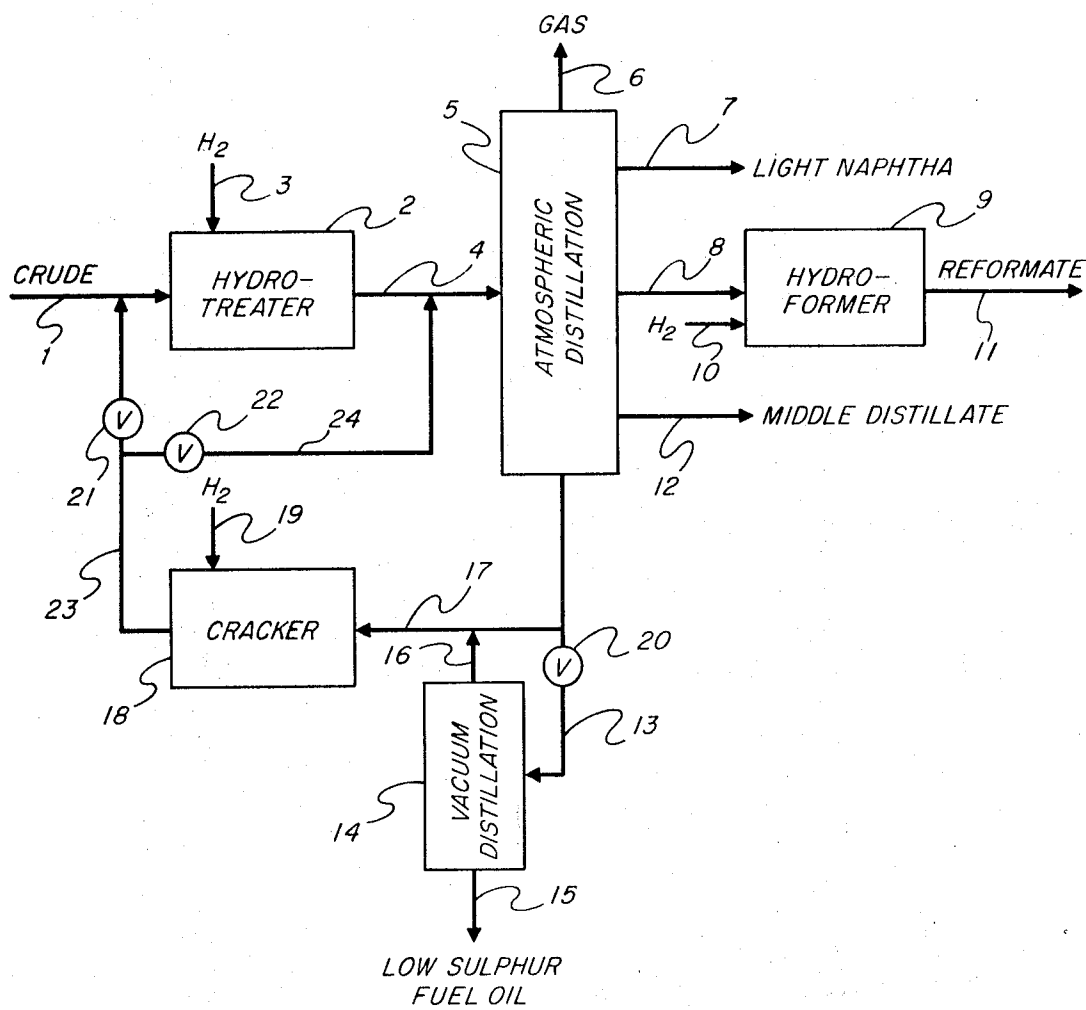
[54] **INTEGRATED PROCESS FOR REFINING WHOLE
CRUDE OIL**
8 Claims, 1 Drawing Fig.
[52] U.S. Cl..... 208/89,
208/97
[51] Int. Cl..... C10g 23/02
[50] Field of Search..... 208/60, 80,
89, 61, 57, 97

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ABSTRACT: The disclosure relates to a process for the refin-
ing of whole crude oil to produce a maximum quantity of
gasoline and distillate products and a minimum quantity of in-
dustrial fuel oil. The process features hydrotreating of whole
crude oil as the first major processing step.





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INTEGRATED PROCESS FOR REFINING WHOLE CRUDE OIL

The first major processing unit in a conventional petroleum refinery is a crude oil distillation tower. The tower is operated to separate the crude oil into a number of petroleum fractions of selected boiling ranges and these fractions are further refined to provide end products having desired characteristics. Many individual fractions are treated with hydrogen and a catalyst to reduce their sulfur content and for other purposes. For this reason, it is not uncommon for a modern petroleum refinery to have five or six different hydrotreating or hydrofining units.

A refinery processing scheme is described in this disclosure which will consolidate all of the hydrogen treating operations, except hydrocracking and hydroforming, in a single unit. The disclosed process is also designed to produce by cracking a maximum quantity of petroleum oil boiling at less than about 1,100° F., which drastically reduces the quantity of low value fuel oil produced in the refinery.

In the process, whole crude is hydrosulfurized to produce a light naphtha fraction suitable for blending into motor gasoline, a heavy naphtha fraction in condition for reforming in the presence of a sulfur sensitive catalyst and one or more desulfurized middle distillate fractions such as kerosene, diesel fuel and home heating oil.

In one preferred embodiment of the process a desulfurized fraction boiling in the gas oil boiling range is hydrocracked to produce a maximum quantity of motor fuel components. In another preferred embodiment a desulfurized fraction boiling in the gas oil boiling range is catalytically cracked to provide a desired product slate including light naphtha, reformer feed stock and distillate fractions boiling in the range of 300° to 750° F.

There are numerous advantages for the refinery processing scheme described herein over a conventional refinery. One hydrotreating unit replaces the light naphtha caustic treater, the hydrofiner associated with the reformer, the virgin and cracked gas oil hydrofiners and the residual oil hydrogenation unit. Reduced sulfur corrosion and consequent maintenance savings are achieved. The overall fuel oil production of the refinery is decreased and any fuel oil that is produced is low in sulfur. The motor gasoline produced is low in sensitivity and lead response is improved. The number of refinery processing units is reduced to a minimum and they are closely integrated for flexibility.

Further objects and advantages of the process of the invention will be apparent from the following description and examples. The flow sheet discloses one of the most preferred embodiments of the invention.

In brief summary, the process comprises catalytically hydrotreating a whole petroleum crude oil to remove sulfur, nitrogen, metals and other contaminants and passing the treated crude to an atmospheric distillation zone. Naphtha and distillate fractions are recovered as products. A fraction boiling in the range of from about 180° to 375° F. is passed to a reforming zone. The atmospheric bottoms fraction is passed to a vacuum tower. The vacuum overhead is passed to a cracker which may be a cat cracker or a hydrocracker. The vacuum bottoms fraction is recovered as low sulfur fuel oil.

Suitable feed stocks for the refining process of the invention comprise whole crude oil fractions, i.e., petroleum fractions which have had no treating except perhaps desalting and removal of light ends. The crude oil will have an initial boiling point in the range of 0° to 100° F. and a 90 percent boiling point in the range of 900° to 1,200° F. The oil will contain from about 0.1 to 8 weight percent sulfur, preferably 0.5 to 4.0 weight percent sulfur, in the form of sulfur compounds such as mercaptans, sulfides, thiophenes etc. The oil may also contain nitrogen in the form of nitrogen compounds, phenols, naphthenic acids, organometallic compounds and asphaltenes.

Referring to the drawing, a sulfur-containing whole crude oil is passed by line 1 to hydrotreater 2. The oil is preferably preheated by means, not shown, to a temperature in the range

of 550° to 800° F. A hydrogen-containing gas containing 70 to 100 percent hydrogen is supplied by line 3.

Typical hydrotreating conditions are set forth below in table I

TABLE I

Hydrotreating Conditions

	Broad	Preferred
Temperature, °F.	550-850	650-775
Pressure, p.s.i.g.	200-5,000	300-2,000
Space Velocity, v./hr./v.	0.1-10	0.2-2
Gas rate, SCF/Bbl.	300-5,000	500-2,000

Suitable hydrotreating catalysts comprise one or more hydrogenation metals supported on a suitable carrier material. The metals can be metals per se but preferably they are in the form of metal oxides or metal sulfides. Salts of Group VI and Group VIII metals are the preferred hydrogenating components. Specifically, oxides or sulfides of molybdenum, tungsten, cobalt, nickel and iron are used. Alumina, alumina containing 1 to 10 weight percent silica, bauxite, kieselguhr, etc., are suitable support materials. The most preferred catalysts are sulfided cobalt molybdate or sulfided nickel molybdate on alumina or silica alumina. The catalyst can be employed in the form of a fixed bed, a slurry or a fluidized bed. Liquid phase or mixed phase conditions are used in the hydrotreater.

The hydrotreating step performs several functions, including hydrosulfurization, hydrosweetening, saturation of olefins, hydrodenitrogenation, etc. Catalyst and reaction conditions are selected in accordance with the characteristics of the crude oil feed and the type and quantity of products desired. For example, if a maximum amount of the gas oil boiling in the range of 650° to 1,050° F. is to be hydrocracked, severe hydrotreating conditions are used to reduce the sulfur and nitrogen content of the gas oil to the lowest possible level. However, if a fairly narrow fraction is to be hydrocracked or catalytically cracked in the presence of a nitrogen tolerant synthetic zeolite catalyst, it may be possible to use less severe hydrotreating conditions.

The hydrotreated whole crude is passed by line 4 to atmospheric distillation tower 5. Conventional means, not shown in the flow sheet, are used to purify hydrotreater hydrogen for recycle. A gas fraction is recovered from tower 5 by line 6. A light naphtha fraction boiling in the range of 75° to 180° F. is recovered by line 7. This fraction is in condition for blending into motor fuel without further treatment such as sweetening and stabilization. A heavy naphtha fraction boiling in the range of from about 180° to 375° F. is passed by line 8 to hydroformer 9.

The hydroformer (reformer) is operated in the conventional manner. Typical hydroforming conditions are set forth below in table II.

TABLE II

Hydroforming Conditions

	Broad	Preferred
Temperature, °F.	880-1,000	900-970
Pressure, p.s.i.g.	50-1,000	100-750
Space Velocity, v./hr./v.	0.5-5	0.5-5
Recycle gas rate, SCF/Bbl.	1,000-10,000	2,000-5,000

Conventional catalysts are employed. Suitable hydroforming catalysts comprise metals selected from the group consisting of molybdenum, chromium, platinum and palladium on alumina. Hydrogen is produced in the reforming operation and part of it is recycled back to the reformer by line 10. Excess reformer hydrogen can be used in hydrotreating and/or hydrocracking. Reformate is recovered by line 11. Platinum and palladium hydroforming catalysts are quickly deactivated by sulfur containing feeds. It is a feature of this invention that the reforming feed fraction is desulfurized as a part of the whole crude and thus no separate hydrofiner is needed to process this fraction.

A middle distillate fraction boiling in the range of 300° to 750° F. is recovered from the atmospheric distillation tower by line 12. If desired, a number of middle distillate fractions such as kerosene, diesel fuel and home heating oil can be recovered. The fractions have already been hydrofined by treatment in the hydrotreater.

The desulfurized bottoms fraction from atmospheric distillation tower 5 having an initial boiling point in the range of about 650° to 750° F. is passed by line 13 to vacuum distillation tower 14. The purpose of the vacuum tower is to make a fairly precise split of the bottoms fraction into cracker feed and a low sulfur fuel oil product fraction recovered by line 15. The cracking feed is passed by lines 16 and 17 to cracker 18. As stated previously, the cracker can be a catalytic cracker or hydrocracker depending on the feed and the type of product slate desired. Assuming hydrocracking is the desired reaction in unit 18, a fraction boiling in the range of about 650° to 950° F. is passed by lines 16 and 17 to the hydrocracker. Hydrogen is supplied by line 19. Hydrogen purification means of any conventional type are employed, but these have not been shown in the flow sheet.

Typical hydrocracking conditions are set forth below in table III.

TABLE III

Hydrocracking Conditions

	Broad	Preferred
Temperature, °F.	600-800	650-750
Pressure, p.s.i.g.	500-5,000	1,000-3,000
Space velocity, v./hr./v.	0.1-5	0.5-2
Gas rate, SCF/Bbl.	1,000-20,000	5,000-10,000

Suitable hydrocracking catalysts comprise a hydrogenating component and a cracking component. Suitable hydrogenation components comprise metals or metal oxides of Groups VI and VII of the Periodic Table, and particularly platinum, palladium, nickel, tungsten and mixtures thereof. Suitable cracking components comprise silica-alumina, silica-magnesia, silica-zirconia, and other amorphous bases, but the most preferred cracking bases for hydrocracking are the crystalline aluminosilicate zeolites known as molecular sieves. A specific example is Zeolite Y, which is commercially available from the Linde Division of Union Carbide Corporation. Since the feed has already been treated in the hydrotreater to remove sulfur and nitrogen contaminants, a single-stage hydrocracker can be employed rather than a two-stage system in which the first stage is relied on to hydrofine the feed. Extinction recycle can be employed for materials boiling above about 450° F.

Hydrocracker effluent comprising gas, a light naphtha fraction boiling in the range of about C₅-180° F. and a heavy naphtha fraction boiling in the range of about 180° to 430° F. is passed by lines 23, 24 and 4 to atmospheric distillation tower 5. Thus, a single atmospheric distillation tower 5. Thus, a single atmospheric distillation tower serves both the hydrotreater and the cracker. Extinction recycle can be employed for the heavy ends from the hydrocracker if desired.

In another preferred embodiment the entire atmospheric bottoms fraction in line 13 is hydrocracked. In this embodiment the vacuum distillation tower is bypassed by closing valve 20 and passing the bottoms directly into the hydrocracker via line 17.

When the refinery is being operated to provide significant amounts of middle distillates, cracker 18 is a catalytic cracker. In this case, line 19 for hydrogen addition would not be required. The vacuum distillation tower is operated to produce a desulfurized vacuum overhead fraction boiling in the range of 650° to 1,050° F. Typical catalytic cracking conditions are set forth below in table IV.

TABLE IV

Catalytic Cracking Conditions

	Broad	Preferred
Temperature °F.	850-1,000	900-950
Pressure, p.s.i.g.	0-50	5-25
Space velocity, v./hr./v.	0.5-10	1-5

Suitable conventional cracking catalysts include amorphous types and mixtures of amorphous types with molecular sieves. Specific examples include silica-alumina, silica-magnesia, silica-zirconia and silica-alumina mixed with a minor proportion of a synthetic crystalline aluminosilicate zeolite such as Type X or Type Y Zeolite.

It is known that catalytic cracking produces olefin hydrocarbons which are not desirable in gasoline. These may be saturated by passing the cracked products through hydrotreater 2. In this embodiment valves 21 and 22 are manipulated to pass all or part of the cracked products via line 23 into line 1 and then into the hydrotreater. The saturated olefins are then recovered from the atmospheric distillation tower.

EXAMPLE I

This example describes hydrotreating of 50,000 B/SD Rainbow crude oil in conjunction with catalytic cracking of the hydrotreated gas oil from the crude. The gas oil boils in the range of 650° to 1,050° F. The object of the example is to demonstrate the production of products that are acceptable without further treatment for processing in a catalytic hydroformer and for blending into motor gasoline, heating oil and heavy fuel oil.

The hydrotreating operation is carried out at preferred conditions of 700° F., 800 p.s.i.g and 1.0 LHSV (based on total volume of crude and cracked distillate), and 1000 s.c.f. of hydrogen per barrel of oil. The catalyst is sulfided cobalt molybdate supported on silica-stabilized alumina.

Table V below shows the characteristics of the crude oil as well as the characteristics of the naphtha, reformer feed and middle distillate cuts obtained from fractionating the hydrotreated oil.

TABLE V

	Column			
	1	2	3	4
Stock.....	Rainbow crude oil	Light naphtha blend	Reformer feed blend	Middle distillate blend
B/SD.....	50,000	6,100	14,600	20,450
Cut point, ° F.....		87/175	175/375	375/700
API gravity.....	42	84	54	35
Sulfur, weight percent.....	0.71	11	13	0.10
Meraptan number.....		Nil		0.5
Nitrogen.....			11	
RON Cl.....		67.8		
P1 us 3 cc. TEL.....		87.8		
MO N Cl.....		68.5		
P1 us 3 cc. TEL.....		86.8		
Pour point, ° F.....				0

¹ Parts per million.

The light naphtha is free of mercaptans and has a high octane response to tetraethyl lead because of its low sulfur content. The reformer feed contains only 3 p.p.m. of sulfur and 1 p.p.m. of nitrogen. Because of these low sulfur and nitrogen levels, this material is suitable for direct reforming in the presence of a platinum catalyst without the usual hydrofining treatment. The middle distillate fraction contains only 0.10 weight percent sulfur and thus the sulfur content is well below the requirements necessary for minimizing air pollution.

Table VI lists the quality data for 13,900 barrels per day of catalytic cracking feed and 4,100 barrels of vacuum pitch obtained from 50,000 barrels a day Rainbow crude. Cracking catalysts are very sensitive to nitrogen and this cracking feed contains only about 0.06 weight percent nitrogen. Metals are also very low, assuring minimum catalyst contamination in this respect. The preferred cracking conditions are 900° to 950° F. reactor temperature, 5 to 20 p.s.i.g. pressure, a regeneration temperature of 1,100° F. and a space velocity of 1 to 5 WHSV. The conversion to naphtha and lighter materials is about 60 percent the conversion to materials boiling at less than 700° F. will exceed 98 percent. The pitch is a suitable low sulfur fuel oil or fuel oil component for blending.

TABLE VI

Column	1	2
Stock	Cat Feed	Pitch
B/SD	13,900	4,100
Cut Point, °F.	700/1,050	1,050+
API Gravity	27	18
Sulfur, Wt. %	0.30	0.74
Nitrogen Wt. %	0.06	
Metals, Iron p.p.m.	0.3	6
Nickel	0.1	4
Vanadium	0.1	2
Conradson Carbon	0.09	11.4
Aromatic Rings, Wt. %	7.9	

EXAMPLE 2

This example describes hydrotreating a blend of 35 percent Federated crude, 35 percent Rainbow crude, 15 percent Pembina and 15 percent Redwater crude. The 650° to 950° F. hydrotreated gas oil fraction is cracked without additional hydrofining. Hydrotreating conditions are more severe than those of example 1. Preferred conditions are 700° F., 1,500 p.s.i.g., 0.8 LHSV and 2,500 s.c.f. hydrogen per barrel. The catalyst is preferably sulfided nickel molybdate on an alumina support. Quality data on the crude oil blend on the fractions from the hydrotreated crude are given in table VII. The light naphtha and middle distillate fractions are acceptable for blending into finished products. The hydrotreated gas oil is hydrocracked at 720° F., 1,500 p.s.i.g. pressure, 1.5 v./v./hr. space velocity and 6,000 s.c.f. H₂/B. The catalyst is preferably nickel tungsten on faujasite. The hydrocracked product is distilled in admixture with the hydrofined crude oil.

TABLE VII

Stock	Column			
	1	2	3	4
	Crude blend	Light naphtha	Reformer feed	Middle distillate
B/SD	50,000	7,410	21,620	15,440
Cut point, °F.		C ₅ /180	180/375	375/650
API gravity	40.2	83	55	37
Sulfur, wt. percent	0.38	Nil	11	0.08
Mercaptan number		Nil	11	0.1
Nitrogen		71		
RON CI		90		
Plus 3 cc. TEL		69		
MON CI		89		
Plus 3 cc. TEL				
Pour point	+20			-10

¹ Parts per million.

The integrated processing scheme described herein consolidates all hydrofining operations in a single unit substantially reducing investment and operating costs.

What is claimed is:

1. An integrated process for producing light naphtha and heavy naphtha from whole petroleum crude oil comprising the steps of:

- passing said whole petroleum crude oil containing sulfur, nitrogen and metal impurities directly to a hydrofining zone;
- hydrofining said crude oil in the presence of a hydrofining catalyst and hydrogen;
- passing hydrofined crude oil to an atmospheric distillation zone;
- distilling an admixture of said hydrofined crude oil with cracked products as hereinafter identified;
- recovering a light naphtha fraction from said distillation zone, and fraction being essentially free of mercaptans;
- recovering a low sulfur, heavy naphtha reformer feedstock fraction from said distillation zone;
- passing a low sulfur, low nitrogen cracking feed fraction from said distillation zone to a cracking zone;
- cracking said fraction in the presence of a sulfur and nitrogen-sensitive cracking catalyst, and
- passing at least a part of the cracked products to the atmospheric distillation zone of step (c) to provide said admixture of step (d).

2. An integrated process for producing light naphtha, heavy naphtha and a fuel oil fraction from whole petroleum crude oil comprising the steps of:

- passing said whole petroleum crude oil containing sulfur, nitrogen and metal impurities directly to a hydrofining zone;
- hydrofining said crude oil in the presence of a hydrofining catalyst and hydrogen;
- passing hydrofined crude oil to an atmospheric distillation zone;
- distilling an admixture of said hydrofined crude oil with hydrocracked products as hereinafter identified;
- recovering a light naphtha fraction from said distillation zone, said fraction being essentially free of mercaptans;
- recovering a low sulfur, heavy naphtha reformer feedstock fraction from said distillation zone;
- passing a low sulfur, low nitrogen atmospheric distillation bottoms from said distillation zone to a vacuum distillation zone;
- recovering a low sulfur fuel oil and cracking feed fraction from said vacuum distillation zone;
- passing said cracking feed fraction to a hydrocracking zone;
- hydrocracking said fraction at a temperature in the range of 650° to 750° F. and a pressure in the range of 1,000 to 3,000 p.s.i.g. in the presence of 5,000 to 10,000 s.c.f./B of hydrogen and a catalyst comprising a metal hydrogenation component and a crystalline aluminosilicate zeolite;
- recovering hydrocracked products comprising a major amount of naphtha, and
- passing said hydrocracked products to the atmospheric distillation zone of step (c) to provide said admixture of step (d).

3. Process according to claim 11, in which the hydrofining catalyst is cobalt molybdate on alumina.

4. Process according to claim 1, in which said cracking feed fraction of step (i) boils in the range of about 650° to 950° F.

5. Process according to claim 1, in which the catalyst of step (j) comprises a nickel-tungsten hydrogenation component on a support comprising zeolite Y.

6. An integrated process for producing light naphtha and heavy naphtha from whole petroleum crude oil comprising the steps of:

- passing said whole petroleum crude oil containing sulfur, nitrogen and metal impurities directly to a hydrofining zone;
- hydrofining said crude oil in the presence of a hydrofining

- catalyst and hydrogen;
- c. passing hydrofined crude oil to an atmospheric distillation zone;
 - d. distilling an admixture of said hydrofined crude oil with cracked products as hereinafter identified; 5
 - e. recovering a light naphtha fraction from said distillation zone, said fraction being essentially free of mercaptans;
 - f. recovering a low sulfur, heavy naphtha reformer feed stock fraction from said distillation zone;
 - g. passing a low sulfur, low nitrogen cracking feed fraction 10 from said distillation zone to a cracking zone;
 - h. catalytically cracking said fraction at a temperature in the range of 900° to 950° F. and a pressure in the range of 5 to 25 p.s.i.g. in the presence of a cracking catalyst comprising a crystalline aluminosilicate zeolite component composited with an amorphous silica alumina component; 15
 - i. recovering catalytically cracked products;
 - j. passing a major proportion of said cracked products to the hydrofining zone of step (b) for saturation of olefins in the cracked products, and 20
 - k. passing a minor proportion of said cracked products to the atmospheric distillation zone of step (c) to provide said admixture of step (d).
7. Process according to claim 6 in which the hydrofining catalyst of step (b) is nickel molybdate on a support comprising alumina and 1 and 10 weight percent silica. 25
8. An integrated process for producing light naphtha, heavy

naphtha and fuel oil from whole petroleum crude oil comprising the steps of:

- a. passing said whole petroleum crude oil containing sulfur, nitrogen and metal impurities directly to a hydrofining zone;
- b. hydrofining said crude oil in the presence of a hydrofining catalyst and hydrogen;
- c. passing hydrofined crude oil to an atmospheric distillation zone;
- d. distilling an admixture of said hydrofined crude oil with cracked products as hereinafter identified;
- e. recovering a light naphtha fraction from said distillation zone, and fraction being essentially free of mercaptans;
- f. recovering a low sulfur, heavy naphtha reformer feed stock fraction from said distillation zone;
- g. passing a low sulfur, low nitrogen atmospheric distillation bottoms from said distillation zone to a vacuum distillation zone;
- h. recovering a low sulfur fuel oil and a cracking feed fraction from said vacuum distillation zone;
- i. cracking the cracking feed fraction of step (h) in a cracking zone in the presence of a cracking catalyst;
- j. passing at least a part of the cracked products to the atmospheric distillation zone of step (c) to provide said admixture of step (d).

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