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(54) **Processing of aromatic vacuum gas oil for jet fuel production.**

(57) Premium jet fuel is produced by dewaxing aromatic vacuum gas oil boiling above the specification for jet fuel over zeolite beta and fractionating the dewaxed material to produce a kerosene fraction boiling in the jet fuel range. Conventional hydrotreating of the kerosene fraction produces a premium jet fuel product.

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PROCESSING AROMATIC VACUUM GAS OIL FOR JET FUEL PRODUCTION

This invention relates to the production of premium jet fuel from aromatic vacuum gas oil.

Refining petroleum crude oils to obtain jet fuel is well known. The jet fuel must meet certain specifications for freeze point, pour point, smoke point and weight percent sulfur. It may be necessary to subject these fuels to additional processing to meet required specifications.

In U. S. Patent No. 4,501,926 to LaPierre et al, gas oil and H_2 contact zeolite beta catalyst to selectively isomerize the paraffinic waxy components in a gas oil feed. U. S. Patent No. 4,501,926 discloses other useful feedstocks, including crude oils, kerosenes, jet fuels, lubricating oil stocks, heating oils and other distillate fractions, whose pour point and viscosity need to be maintained within certain specification limits.

However, although a pour point specification may be met by the above, the sulfur in the product may exceed specifications, thus requiring additional processing, typically in a hydrotreater.

U. S. Patent No. 3,573,198 to Parker et al teaches smoke point improvement of jet fuel kerosene fractions by treating a sulfurous kerosene fraction by a two-stage process. The first stage principally desulfurizes and the second stage principally saturates aromatics by contact with a catalystic of alumina, a halogen component, a Group VIII noble metal component and a Group VII-B metallic component. U. S. 3,573,198 does not suggest upstream processing most appropriate for combination with its process. Highly olefinic/aromatic kerosene is the least desirable feed for this process.

U. S. Patent No. 4,427,534 to Brunn et al discloses production of jet and diesel fuels from highly aromatic oils using a sulfided, halogen-promoted Group VIB-Group VIII metal on an alumina-containing support. The process has the disadvantage that it employs hydrocracking, which opens aromatic molecules to form paraffinic material. By opening aromatic rings, the hydrocracked products can have a higher pour point than the feed to hydrocracking.

To produce high quality jet fuel from vacuum gas oil, containing 20 to 50 wt. % aromatics requires severe operating conditions, such as high pressure, to treat aromatic chargestocks by hydrocracking. Hydrocracking can increase pour point. It would be desirable to produce jet fuel at moderate pressure from aromatic chargestocks. This is particularly significant since it is projected that refineries will process a higher proportion of heavy crudes, which are typically aromatic.

Accordingly, the present invention provides a process for producing jet fuel from a vacuum gas oil feed having at least 20 to 50 wt % aromatics and boiling above 343°C (650°F) by contacting the feed with a dewaxing catalyst comprising a hydrogenation component and zeolite beta having a silica:alumina ratio of at least 30:1 at 199-538°C (390° to 1000°F), a pressure of atmospheric to 10,400 kPa (1500 psig), a liquid hourly space velocity of 0.2 to 5.0 hr^{-1}, in the presence of hydrogen to produce a dewaxed effluent stream, wherein most aromatics in the feed are unchanged; separating the dewaxed effluent stream into a kerosene fraction containing hydrocarbons boiling below 343°C (650°F) and a heavier fraction; hydrotreating the kerosene fraction with a conventional hydrotreating catalyst under conventional hydrotreating conditions to produce a hydrotreated kerosene stream; and recovering from the hydrotreated kerosene stream a jet fuel product.

The process of the present invention produces jet fuel having a low freeze point and low pour point from a vacuum gas oil boiling above 288°C (550°F) preferably above 343°C (650°F). Vacuum gas oils typically boil in the range from 288 to 566°C (550° to 1050°F), more usually 343 to 454°C (650° to 850°F). Furthermore, the process of the present invention produces jet fuel from highly aromatic (at least 20-50 wt % aromatics) feeds with minimal conversion of aromatics during isomerization of paraffins into jet fuel hydrocarbons, thus improving jet fuel quality by not converting the aromatics into higher pour point paraffins. The process also improves jet fuel quality by mild hydrotreating of the kerosene cut separated from other hydrocarbons in the effluent from isomerization, thus allowing easy processing to produce a jet fuel which meets jet fuel specifications for aromatics content, pour point, freeze point, sulfur content and smoke point.

The figure illustrates isomerization dewaxing followed by hydrotreating of a kerosene fraction.

The vacuum gas oil feed comprises aromatics, paraffinic, waxy components and sulfur compounds. The vacuum gas oil stream 12 is combined with a hydrogen stream 14 to form a combined stream 16. Typically the vacuum gas oil comes from a vacuum distillation tower (not shown). The combined stream 16 passes into reactor 20, preferably a co-current downflow trickle bed reactor. Feed contacts catalyst comprising a hydrogenation component and zeolite beta to produce a dewaxed effluent stream 22. The aromatics are substantially unchanged in the dewaxing unit 20. The preferred isomerization conditions are a temperature of 199 to 538°C (390° to 1000°F), a pressure of atmospheric to 10,400 kPa (1500 psig), a liquid hourly

space velocity (LHSV) from 0.2 to 5.0 hr^{-1} and a hydrogen feed rate of 90 to 900, n l/l, normal liters per liter of liquid feed (500 to 5000 SCF/bbl of vacuum gas oil). Most preferably, the temperature is 371 to 454 - (700° to 850°F), the pressure is 2200 to 3500 kpa (300 to 500 psig) the liquid hourly space velocity is 0.5 to 2.0 hr^{-1}, and the hydrogen feed rate is 180 to 540 n l/l (1000 to 3000 SCF/bbl).

The dewaxed effluent is separated by separator 30 into a vapor stream 34 and a liquid stream 36. The vapor (H_2 and C_1-C_4 hydrocarbons) may be recycled, used as fuel gas or separately processed. The liquid, comprising C_5+ hydrocarbons, enters distillation tower 40 which produces a naphtha stream 42, typically C_5 to 143°C (290°F) a kerosene stream 46 and a bottoms stream 44. The aromatics impair the subsequent hydrotreating of the kerosene. Tower 40 facilitates downstream hydrotreating of the kerosene because the aromatics (which are not changed much in reactor 20) are still high boiling and concentrate in the bottoms stream 44. The kerosene stream 46 is combined with hydrogen from stream 48 to form a hydrotreater feed stream 49, which enters hydrotreater 50.

The kerosene 46 has some olefins and sulfur compounds. The hydrotreater 50 removes some of the sulfur and saturates some of the olefins. Hydrotreater 50 contains conventional hydrotreating catalysts, and operates at conventional conditions.

Typically the hydrotreater operates at 1800 to 5600 kPa (250 to 800 psig), a temperature of 240 to 427°C (400° to 800°F), a liquid hourly space velocity from 0.5 to 10.0 hr^{-1}, and a hydrogen feed rate of 90 to 900 n l/l (500 to 5000 SCF/bbl). The hydrotreated effluent stream 52 passes from hydrotreater 50 into separator 60 which separates stream 52 into a C_4-vapor stream 64 and a C_5+ liquid stream 66.

The liquid stream 66 passes to a stripper 70. The hydrotreated liquid is preferably steam-stripped by steam, from line 72 into a naphtha stream 74 and a jet fuel stream 76. The jet fuel stream 76 typically comprises 143 to 288°C (290° to 550°F) hydrocarbons.

Preferably, the jet fuel stream 76 has a smoke point within 1 mm of the smoke point of the kerosene stream 46. The jet fuel, stream 76, preferably meets jet fuel smoke point specifications, and may be blended into the refinery jet fuel pool.

Boiling point of the jet fuel is related to freeze point. The higher boiling point components have higher freeze points than the lower boiling point components. Distillation cut points can be adjusted by conventional means, e.g., by changing fractionator reflux rates, temperatures, etc. For jet fuel, the freeze point may range from -40° to -50°C (-40° to -58°F).

The isomerization dewaxing catalyst comprises zeolite beta with a hydrogenation component. Zeolite beta is described in U.S. Patent Nos. 3,308,069 and Re. 28,341. Isomerization dewaxing is described in U.S. 4,412,220.

The hydrotreating catalyst and process are conventional. Typically the hydrotreating catalyst is Ni, Mo, Co, W, NiMo, CoMo, etc., on an amorphous support such as alumina.

This invention will be illustrated by the examples. Dewaxing and hydrotreating were run in a 100 cc downflow fixed bed test reactor. The test reactor had a 2.5 cm (1-inch nominal) inside diameter and a 91 cm (36-inch) length, including a 30 cm (12-inch) preheater, a 30 cm (12-inch) catalyst space and a 30 cm - (12-inch) bottoms space. 75 cc of catalyst was used. H_2 was added at a rate of 360 nl/l (2000 SCF/bbl).

Examples 1-5 illustrate prior art processes (Examples 1-4) or processes which do not form part of the state of the art but which are not claimed as the invention (Example 5).

Example 1(Prior Art)

The feed properties are shown below.

TABLE 1

Boiling range °C	204-371	343-454
Boiling range °F	400-700	650-850
Gravity, °API	34.5	25.1
Density g/cc	0.852	0.904
Hydrogen, Wt %	13.50	12.53
Sulfur, Wt %	1.43	2.16
Nitrogen, ppm	110	540
Compositions, Wt %		
Paraffins, Wt %	43.9	29.0
Naphthenes	24.3	25.5
Aromatics	31.8	45.5
Distillation, °C/°F		
5%	214/418	349/660
10%	233/452	358/676
50%	303/577	403/758
90%	364/687	448/838
95%	374/706	457/854

The 204-371°C (400-700°F) fraction is a typical light gas oil.

The 343-454°C (650-850°F) fraction is a typical aromatic vacuum gas oil, and is preferred feedstock for use in the present invention.

Example 2 (Prior Art)

This example reports catalyst properties of two hydrotreating catalysts and one isomerization dewaxing catalyst.

TABLE 2

Catalyst Properties

Catalyst	Al_2O_3/NiMo	Al_2O_3/CoMo	Pt/Zeolite Beta
Chemical Compositions			
Pt, Wt %	-	-	0.56
Ni, Wt %	3.5	-	-
Co, Wt %	-	5.0	-
MoO_3, Wt %	20.0	16.2	-
Physical Properties			
Surface Area, m^2/g	135	230	371
Pore Volume, cc/g	0.389	0.52	0.70
Avg. Pore Diameter, Å	113	90	76
Pore Size Distribution, %			
30 Angstroms	12	-	22
30 - 100 Angstroms	67	-	30
100 - 200 Angstroms	10	-	14
200 - 300 Angstroms	1	-	7
300+ Angstroms	10	-	27

The isomerization dewaxing catalyst, platinum zeolite beta, comprised about 35 wt % alumina 65 wt % zeolite beta to which was added 0.56 wt % platinum. The catalyst was prepared by blending 65 wt % zeolite beta and 35 wt % alumina with water. This was then extruded to 1.6m (1/16") outside diameter pellets and dried at 121°C (250°F) in nitrogen. Then, the catalyst was heated at 2.8°C/min (5°F/min) in nitrogen and calcined in nitrogen for 3 hours at 538°C (1000°F) then calcined in air for 3 hours at 538°C - (1000°F). The air-calcined catalyst was steamed 10 hours at 538°C (1000°F) and 1 atm steam pressure. The catalyst was ammonium-exchanged twice at room temperature with 1 normal NH_4NO_3, washed with water and dried at 121°C (250°F) overnight. Then, the catalyst was exchanged for 12 hours at room temperature with $Pt(NH_3)_4Cl_2$, at a concentration of 4 milliliters water per gram of platinum salt, with stirring. The catalyst was then washed 4 times until free of chlorine. The washed catalyst was then dried at 121°C - (250°F) overnight and calcined for 3 hours at 349°C (660°F) in a 60% air, 40% N_2 mixture which has a dew point of -6°C (22°F).

The resulting zeolite beta catalyst had an alpha value of 50 based on zeolite. The significance of the alpha value and a method for determining it are described in U. S. Patent No. 4,016,218 and J. Catalysis, 61, 390-366 (1980). Catalysts having an alpha value based on zeolite of 10 to 150, preferably 10 to 100, or most preferably 30 to 70, are preferred for isomerization dewaxing. Alpha can be changed by steaming, by alkali-exchange or by varying the silica:alumina ratio of the zeolite.

Example 3 (Prior Art)

This example shows what can be achieved by hydrotreating alone, hydrotreating follows by isomerization dewaxing, and isomerization dewaxing alone of Arabian Light Gas Oil

TABLE 3

Process	Hydrotreating	Hydrotreating/ Dewaxing	Dewaxing
Operating Conditions			
Catalyst (1)	$CoMo/Al_2O_3$	$NiMo/Al_2O_3$	Pt/zeolite beta
Catalyst (2)	-	Pt/Zeolite Beta	-
Pressure, psig	500	350	350
kPa	3500	2500	2500
Temperature (1),°C/°F	399/750	399/750	399/750
Temperature (2),°C/°F	-	399/750	-
Overall LHSV, Hr^{-1}	0.5	0.5	1.0
Kerosene Properties			
Cut Points, °C	149/260	143/288	143/288
Cut Points, °F	300-500	290-550	290-550
Freeze Point, °C	-39	-40	-39
Freeze Point, °F	-38	-40	-39
Smoke Point, mm	16	13.5	19.5
Diesel Index	37.5	43.4	58.5
Composition			
Saturates, Vol %	45	58	69
Olefins, Vol %		3	4
Aromatics, Vol %	55	39	27

The results show that contacting light gas oil with the platinum zeolite beta catalyst produced in high quality jet fuel.

Example 4 (Prior Art)

This example demonstrates the production of jet fuels from a heavier feed, the vacuum gas oil shown in Table 1. This heavy feed was processed over the platinum zeolite beta catalyst of Example 2. The feed - (vacuum gas oil) is within the scope of the invention but the processing (isomerization dewaxing alone) is not.

The reactor pressure was 2500 kPa (350 psig), the liquid hourly space velocity was 1.0 hr^{-1}, the temperature was 416 to 421°C (780° to 790°F), with 356 nl/l (2000 SCF/bbl) of H_2. The reactor effluent was distilled to produce a 143 to 288°C (290° to 550°F) fraction, equivalent to stream 46 of the figure. Table 4 lists the properties of the 143°C$^+$ (290°F$^+$) effluent and its 143 to 288°C (290° to 550°F) fraction. The 143 to 288°C (290° to 550°F) fraction meets smoke point requirements, but has too much sulfur (0.67 wt %) and olefins (7.7 vol %).

TABLE 4

Isomerization-Dewaxing of Vacuum Gas Oil

Product Fraction	143°C$^+$ 290°F$^+$	143-288°C 290-550°F
Gravity, °API	30.0	43.3
Density, g/cc	0.876	0.809
H, Wt %	13.04	13.76
S, Wt %	1.39	0.67
Pour Point, °C/°F	-32/-25	-54/-65
Freeze Point, °C/°F	--	-42/-43
Diesel Index	44.1	58.2
Smoke Point, mm	--	19.0
KV at 40°C, CS	3.692	1.363
KV at 100°C, CS	1.389	0.711
Liquid Volume %		
Saturates	--	65.4
Olefins	--	7.7
Aromatics	--	26.9
Distillation, °C/°F		
5%	149/301	124/256
10%	173/343	142/288
30%	242/468	186/367
50%	296/565	223/434
70%	372/702	252/486
90%	419/786	281/538
95%	434/814	290/554

Example 5 (Comparison Test)

This example demonstrates isomerization-dewaxing followed by hydrotreating of the entire effluent. The entire 143°C$^+$ (290°F$^+$) effluent from the test reactor is hydrotreated using the conventional $NiMo/Al_2O_3$ hydrotreating catalyst listed in Table 2. The effluent from hydrotreater was distilled to form a jet fuel fraction 143 to 288°C (290° to 550°F) whose properties are summarized in Table 5. Hydrotreating the entire 143°C (290°F$^+$) dewaxing reactor effluent degraded the jet fuel as shown by its lower smoke point and higher aromatics content compared to the unhydrotreated 143-288°C (290° to 550°F) fraction produced in Example 4 and listed in Table 4.

Example 6-8 (Invention)

This example demonstrates isomerization-dewaxing of a vacuum gas oil followed by hydrotreating the kerosene fraction of the dewaxed effluent. The dewaxed effluent of Example 4 is fractionated to produce a kerosene fraction of 143 to 288°C (290° to 550°F) representing stream 46 of the figure. This fraction was hydrotreated at varying temperatures using the conventional ($NiMo/Al_2O_3$) hydrotreating catalyst of Table 2. The hydrotreated material was stripped to recover a jet fuel product of 143 to 288°C (290° to 550°F). Hydrotreating conditions and jet fuel product properties are listed in Table 5.

TABLE 5

Isomerization-Dewaxing Then Hydrotreating

Example	5	6	7	8	
Hydrotreater Feed	Isomerization Effluent	-----Jet Fuel Fraction-----			
Boiling Range	290°F+ / 143°C+	---290° - 550°F Fraction--- / ---143° - 288°C ----------			
Pressure, psig	500	500	500	500	
kPa	3500	3500	3500	3500	
Temperature, °F	702	601	651	700	
°C	372	316	344	371	
LHSV, Hr^{-1}	1.0	1.0	1.0	1.0	
H_2 Feed Rate, SCF/B	2000	2000	2000	2000	
n/l/l/$^{-1}$	356	356	356	356	
Jet Fuel Product					Jet A Spec.
Gravity, °API	39.6	43	42.4	42.0	31-51
Gravity, g/cc	0.827	0.811	0.814	0.815	0.87-0.78
H, Wt %	13.21	13.95	14.47	13.84	--
S, Wt %	0.006	0.076	0.026	0.02	0.3
Pour Point, °C/°F	-48/-55	-48/-55	-48/-55	-48/-55	--
Freeze Point, °F	-41/-42	-41/-42	-41/-42	-41/-42	-40/-40
Diesel Index	49.7	60.8	60.0	59.4	--
Smoke Point, mm	16.0	19.0	20.0	18.5	18
Naphthalenes, Vol %	2.32	2.03	1.49	2.3	3
Composition, Vol %					
Saturates	62.5	71.2	72.6	71.3	--
Olefins	2.6	1.8	2.2	2.3	--
Aromatics	34.9	27.0	25.3	26.4	25

In Example 5, the entire 143°C+ (290°F+) isomerization dewaxing reactor effluent is hydrotreated. Even though the boiling range of the jet fuel product is the same (because of fractionation to obtain a 143 to 288°C product) in Examples 5-8, the jet fuel made in Example 5 is not as good as the jet fuel made in Examples 6-8.

Increasing the hydrotreating temperature from 316°C (601°F), in Example 6 to 344°C (to 651°F) in Example 7 gave a jet fuel product having less sulfur and a higher smoke point.

Hydrotreating at 371°C (700°F), in Example 8, gives a jet fuel product with an 18.5 mm smoke point, as opposed to the 20.0 mm smoke point of the product from Example 7.

The results in Table 5 indicate that hydrotreating the jet fuel fraction, the 143-288°C (290° to 550°F) fraction, separately from 288°C (550°F+) components, improves the jet fuel quality, as shown by a higher diesel index, higher smoke point and lower volume percent olefins. The 143-288°C (290° to 550°F) fractions after hydrotreating, as shown in Examples 6-8, can be blended directly into refinery jet fuel pools.

Thus, the present invention provides jet fuel which meets typical freeze point, pour point and smoke point specifications. The process of the present invention can produce jet fuel from 343°C+ (650°F+) feedstocks which are highly aromatic. The process selectively cracks heavy paraffins to jet fuel boiling range materials while it converts little of the heavy aromatics in the feed into the jet fuel fraction. Jet fuel quality is improved by mildly hydrotreating the kerosene cut separately from heavier hydrocarbons. The present invention also removes aromatics from the hydrotreater feedstock by fractionating heavier hydrocarbons away from the kerosene fraction prior to hydrotreating, because aromatics tend to concentrate in the heavier hydrocarbons.

Isomerization-dewaxing, followed by fractionating and hydrotreating, produces high quality jet fuel at low pressures even from chargestocks containing 20 to 50+ wt. % aromatics. This is significant since refineries will process more heavy crudes which contain more aromatics.

Claims

1. A process for producing jet fuel from a vacuum gas oil feed having at least 20 to 50 wt % aromatics and boiling above 343°C (650°F) by contacting the feed with a dewaxing catalyst comprising a hydrogenation component and zeolite beta having a silica:alumina ratio of at least 30:1 at 199-538°C (390° to 1000°F), a pressure of atmospheric to 10,400 kPa (1500 psig), a liquid hourly space velocity of 0.2 to 5.0 hr^{-1}, in the presence of hydrogen to produce a dewaxed effluent stream, wherein most aromatics in the feed are unchanged;
separating the dewaxed effluent stream into a kerosene fraction containing hydrocarbons boiling below 343°C (650°F) and a heavier fraction;
hydrotreating the kerosene fraction with a conventional hydrotreating catalyst under conventional hydrotreating conditions to produce a hydrotreated kerosene stream; and
recovering from the hydrotreated kerosene stream a jet fuel product.

2. The process of Claim 1, further characterized in that the kerosene fraction boils within the range of 143-288°C (290° to 550°F).

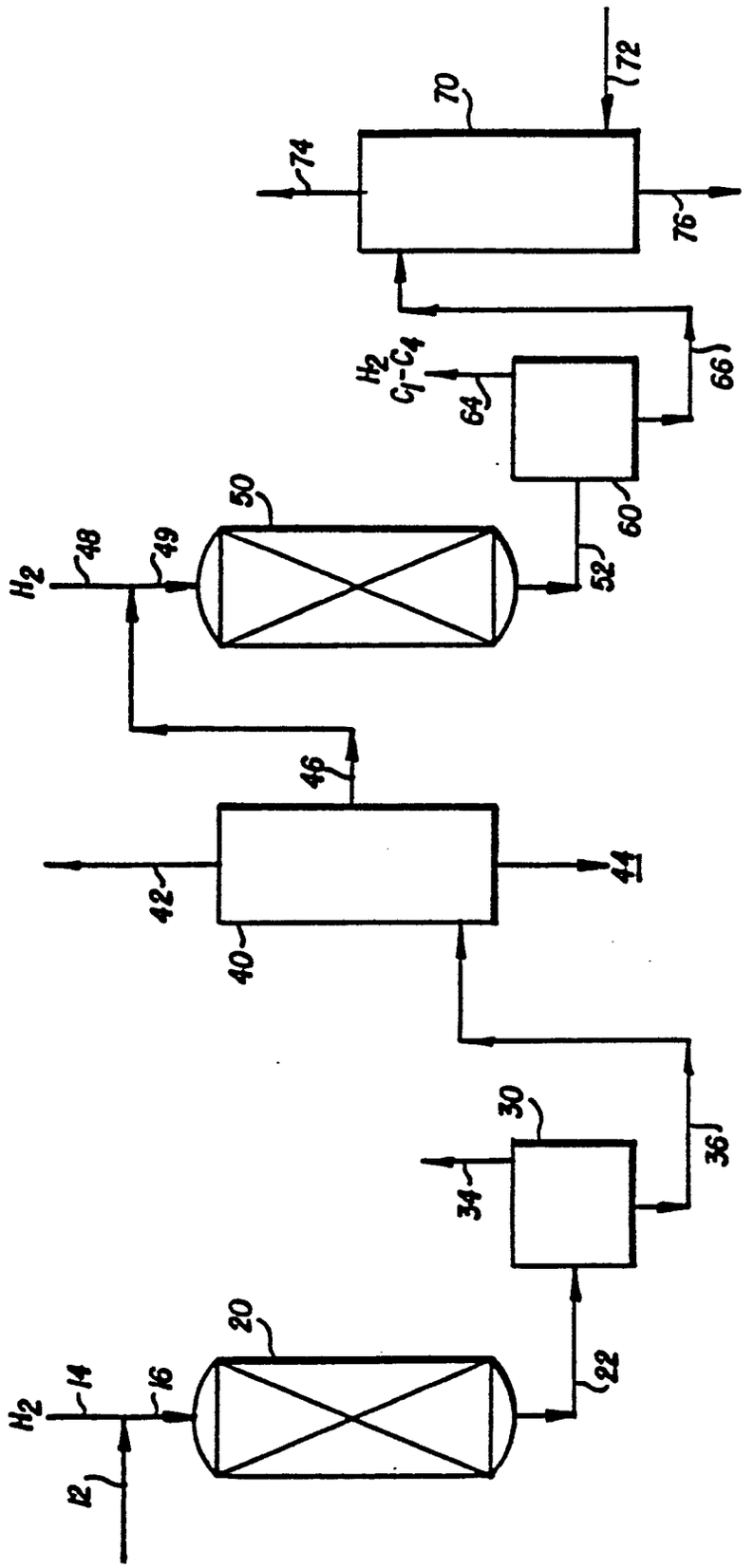
3. The process of Claim 1 or 2 further characterized in that the dewaxing occurs at a pressure from 2200 to 3500 kPa (300 to 500 psig).

4. The process of any preceeding Claim further characterized in that the hydrogenation component of the dewaxing catalyst comprises 0.1 to 5.0 wt % of a noble metal of Group VIII of the Periodic Table.

5. The process of Claim 4 further characterized in that the hydrogenation component is 0.1 to 1.2 wt % platinum.

6. The process of any preceeding Claim further characterized in that the vacuum gas oil feed boils above 343°C (650°F) and contains more weight % aromatics than paraffins.

7. The process of any preceeding Claim further characterized in that the vacuum gas oil contains at least 2.0 wt. % sulfur, the dewaxing step converts a portion of the feed to olefins, the kerosene fraction comprises olefins and sulfur, and the conventional hydrotreating removes a portion of the sulfur, and saturates a majority of the olefins in the kerosene fraction.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