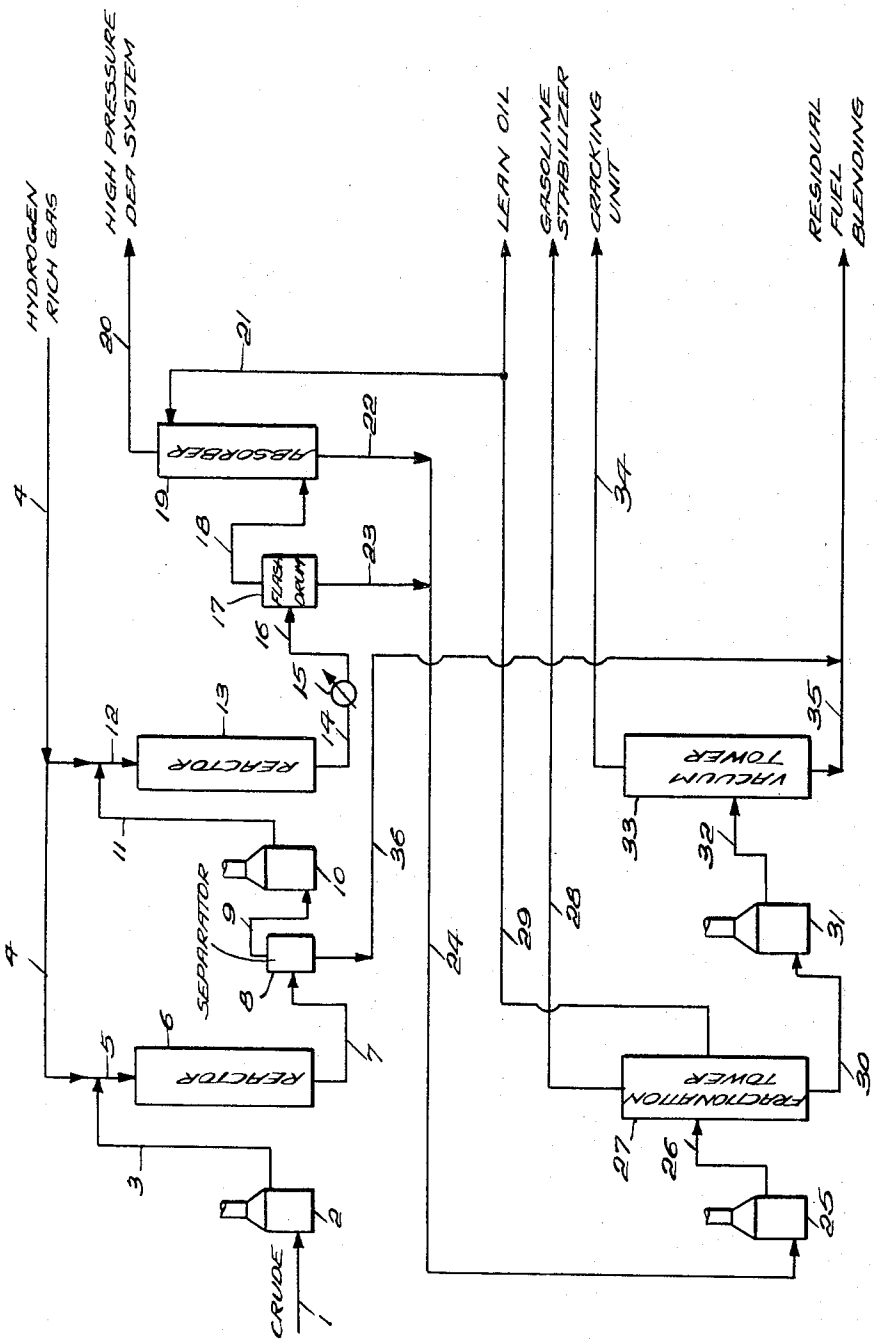
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TWO STAGE HYDROGENATION OF REDUCED CRUDE

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TWO STAGE HYDROGENATION OF REDUCED CRUDE

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ABSTRACT OF THE DISCLOSURE

A process adapted for the removal of asphaltenes, or pentane insolubles, from a feed which is to be hydrogenated and which contains as the essential ingredient, and usually as the predominant component, a reduced crude, boiling primarily in the range between about 650° F. and 1200° F. The present invention is particularly concerned with hydrogen treating reduced crudes containing an undesirable amount of asphaltene, e.g. about 4% or more pentane insolubles in the absence of an added solvent to cause the asphaltenes to agglomerate over a relatively inexpensive and inactive catalyst or an essentially inert material which may be discarded at frequent intercals at small costs to reduce the pentane insolubles by at least 25 wt. percent and preferably about 70 wt. percent.

The present invention relates to a two-stage process for the hydrogenation of reduced petroleum crudes and more particularly relates to the production of a low sulfur, low viscosity residual fuel component or low sulfur, low metal content, gas oil for subsequent treatment in a catalytic cracking unit.

It is recognized that the prior art teaches a single stage treatment of asphalt and reduced asphaltic crude; however, the prior art processes are economically deficient in that the processing cycles have been of short duration and required swing reactors and extensive catalyst regeneration facilities. The petroleum refiner is, therefore, continually seeking new and better processes for the conversion of the heavy ends of petroleum crude oil to more useful products. One such method involves the removal of asphaltenes from the reduced crude. A conventional process for the removal of asphaltic materials, for example, involves solvent extraction. This process is disadvantageous in that special materials, solvent, solvent storage, equipment, etc. are required.

An economical process has, however, now been discovered which provides for the treatment of reduced asphaltic crudes. This process is especially adapted for the removal of asphaltenes and to give increased yields of low sulfur, low pour point, distillate heating oils; a low sulfur, low viscosity residual fuel component; and/or increased quantities of low sulfur, low metal content, gas oil for subsequent treatment in a catalytic cracking unit.

In general, this improved process involves hydrogen pretreating of a feed, i.e. a reduced mineral crude oil-containing feed to cause the asphaltenes present in the reduced crude to agglogerate, for example, over a relatively inexpensive and/or inactive catalyst or an essentially inert material which may be discarded at frequent intervals at small cost. While the mechanism of treatment using an inert or near inert material, i.e., essentially thermal treatment, is somewhat different from an active catalytic treatment, the resultant higher boiling fractions of the effluents and agglomeration or coagulation of the contained asphaltenes is similar. Although it is not intended for the instant process to be limited to any particular theory one possible hypothesis for this agglomeration is that the hydrogenation of peptizing agents, which normally keep asphaltenes in a collodial suspension, takes place with either thermal or catalytic treatment; and, when

the peptizing agents are altered in chemical characteristics, the asphaltenes tend to coagulate or agglomerate. The asphaltenes can be removed from the processing stream after agglomeration in various ways, e.g., by hot filtering, or by flashing off the volatile hydrocarbon materials in which event the asphaltenes end up in the bottoms or as a residue and the volatized processing stream is sent to a second-stage hydrogen treatment. The residue from flashing may be recycled or sent to residual fuel.

The second-stage hydrogen treatment is conducted over a catalyst which preferably is of greater activity than the catalyst or inert material in the first-stage hydrogen pretreating. Depending on the conditions chosen for the second stage, the reduced crude can be desulfurized and also may provide some saturation of aromatic nuclei to yield on subsequent vacuum fractionation, a gas oil with enhanced catalytic cracking properties. Conditions for the second stage can also be chosen so that considerable hydrogenative hydrocracking takes place and, upon subsequent fractionation, yields increased quantities of low sulfur, low pour point distillate heating oil, and a low sulfur residual fuel component.

The feed which is to be hydrogenated in the present invention, in general, contains as the essential ingredient, and usually as the predominant component, a reduced crude, i.e. the high-boiling residue remaining after distillation of a crude oil to remove for example, gasoline, kerosene and light gas oil. Such reduced crudes usually boil predominantly in the range between about 650° F. and 1200° F. although the initial boiling point may sometimes be as low as 600° F. and as high as about 900° F. and the end point may on occasion be as low as about 900° F. and even higher than the 1200° F. mentioned above. Only a small part, e.g. 5.5% to 3% or less, of a reduced crude will usually boil at greater than 1300° F. The present invention is particularly concerned with treating reduced crudes containing an undesirable amount of asphaltenes, e.g. pentane insolubles. Reduced crudes often contain, for example, about 4% or more pentane insolubles, and also, about 25 p.p.m. or more of nickel or vanadium measured as the oxides NiO and V_2O_5, usually about 25 p.p.m. or more of each. In accordance with this invention, the pentane insolubles are generally reduced in the first stage hydrogen treatment by at least about 25 weight percent and preferably by at least about 70%.

Referring now to the first stage hydrogen pretreating or processing of the reduced crude, the first stage catalytic treatment of the present invention is generally conducted over a sulfur-insensitive hydrogenation catalyst such as catalysts containing as the active promoter an iron transition series metal of Group VII of the Periodic Table, for example, cobalt, nickel, and iron, preferably in combination with a Group VI–B metal such as molybdenum or tungsten, and preferably on a support material such as alumina, silica, silica-alumina, magnesia, titania, etc. A typical first stage catalyst contains about 0.5 to 3% by weight of a Group VIII metal and about 2–15% by weight of a Group VI–B metal on a support. An essentially thermal first-stage treatment can also be employed using an essentially inert particulate contact material such as tabular alumina, electrician beads, extruded alumina, etc. or a low activity catalyst.

The reaction conditions employed in the first-stage processing can vary over wide ranges depending on the particular feed and type of material, i.e. catalytic or inert, used. Generally, the conditions include a pressure of from about 100 to 2500 p.s.i.g., preferably from about 500 to 1500 p.s.i.g., and a temperature of about 600° to 900° F., preferably from about 750° to 850° F. The pressure and temperature for a first stage thermal unit are essentially the same as for a catalytic unit; however,

the preferred temperature for a thermal unit is slightly higher, i.e. from about 800° to 900° F. The weight hourly space velocity (WSHV) of the feed in the first stage will generally be from about 0.3 to 5 lbs. feed/hr. pound of catalyst and the hydrogen gas rate will generally be from about 1000 to 10,000 standard cubic feet per barrel (s.c.f./b.) of feed. The preferred WHSV is from about 0.5 to 2 and the preferred hydrogen rate is from about 2500 to 5000 s.c.f./b.

Second-stage hydrogen processing is accomplished over hydrogenation catalysts which preferably are more active than the contact material used for first-stage processing, i.e. catalytic or inert particulate material. Suitable catalysts for second-stage processing also include catalysts containing promoting amounts of a Group VIII iron transition series metal, preferably in combination with other active hydrogenation components such as Group VI–B metals, including tungsten, etc. The promoting metals are generally supported in minor amounts on a suitable carrier such as activated alumina, silica, silica-alumina, magnesia, titania, zirconia, etc. The catalysts used in the second stage often contain about 1 to 10% by weight of Group VIII promoting metal such as cobalt, and, if present, about 8 to 30% by weight of the additional component, e.g. Group VI–B metal such as molybdenum, on alumina and can be prepared by known methods. Since, in general, lower activity catalysts are characterized by lower surface areas, the catalysts of the first and second processing stages may be further distinguished. The catalyst for the first stage will typically have a surface area of from about 50 to 250 $m.^2/gm.$ whereas the catalyst for the second stage can have a surface area in excess of about 250 $m.^2/gm.$

It is preferred that the second-stage catalyst be sulfided before use, for instance, by treatment with H_2S at high temperatures to put the cobalt or other promoting metals in sulfide form; however, the cobalt oxide form, including, for instance, cobalt molybdate can be used. A cobalt-containing catalyst, e.g. cobalt-molybdenum on alumina support is one of the most desirable catalysts for second-stage processing, however, if hydrocracking of the reduced crude is a preferential reaction a nickel containing catalyst, e.g. nickel-molybdenum on a silica-alumina support can be preferable. Furthermore, a sulfur-sensitive hydrogenation catalyst can be used, if desired, for second-stage processing. Such catalysts include those promoted with a Group VIII noble metal, e.g. platinum, palladium, etc. Generally, these metals are present in amounts, e.g. about 0.1 to 5% by weight, on a suitable carrier such as those described above.

Conditions for the second-stage processing directed toward improved catalytic cracking feedstock generally include a pressure of from about 500 to 2500 p.s.i.g., weight hourly space velocity (WHSV) of from about 0.3 to 5; temperature of from about 700 to 800° F.; and hydrogen rate of from about 1000 to 10,000 s.c.f./b. whereas the preferred operating conditions include a pressure of from about 500 to 1500 p.s.i.g., WHSV of from about 0.5 to 1; temperature of from about 720 to 780° F., and hydrogen rate of from about 1000 to 5000 s.c.f./b. Processing conditions directed toward hydrocracking to increase production of middle distillate stocks generally include a pressure of from about 500 to 2500 p.s.i.g.; WHSV of from about 0.3 to 2; temperature of from about 750 to 950° F.; and hydrogen rate of from about 1000 to 10,000 s.c.f./b. The preferred operating conditions directed toward hydrocracking are a pressure of from about 500 to 1500 p.s.i.g., WHSV of from about 0.5 to 1.5; temperature of from about 825 to 925° F.; and hydrogen rate of from about 1000 to 5000 s.c.f./b.

The present invention may be more fully understood from the following description with reference to the attached drawing in which the sole figure is a flow diagram illustrating the instant process. It will be obvious to those skilled in the art that other flow arrangements can be used within the scope of the instant invention, and accordingly this description intended only for purposes of illustration.

Referring now to the drawing, reduced crude is pumped through line **1** to heater **2** where the temperature is raised to the desired level. Heater effluent flows through line **3** where it is contacted in line **5** with a hydrogen-rich gas stream from line **4**. Heated oil hydrogen-rich gas enter a first stage reactor **6** which is filled with catalyst or inert material as described above. Reactor effluent leaves reactor **6** through line **7** and enters separator **8**, e.g. a flash drum, where the fixed gases and gas oil fraction, and boiling below about 1100° F., are taken overhead through line **9**. The bottoms material consisting of material boiling above about 1100° F. and including asphaltenes is sent to residual fuel blending through line **36**. Alternatively, separator **8** may consist of a series of preferably replaceable filters in which case only the agglomerated materials, e.g. asphaltenes, are sent to residual fuel and all normally liquid hydrocarbons enter line **9**. Overhead fractions from line **9** enter heater **10** where they are heated to reaction temperature, depending on the reaction desired as explained above. Heater effluent flows through line **11**, where it is contacted in line **12** with a hydrogen-rich gas fed through line **4**.

The heated hydrocarbons and hydrogen-rich gas then enter reactor **13** which is filled with an active hydrogenation catalyst. Depending upon the desired products, sulfur, carbon residue and metals content are reduced to a desired level or the feed may be hydrocracked to lower boiling hydrocarbons along with reduction in sulfur, carbon residue and metals content. Reactor effluent leaves the reactor through line **14**, passes through heat exchanger **15** where it may be cooled and enters a low temperature flash drum **17** through line **16**. Overhead fractions from this flash drum, consist mostly of hydrogen, methane, and other light gases plus some gasoline. The components of these overhead fractions are preferably separated, e.g. by an absorber **19** which they enter through line **18**. An absorber oil, e.g. boiling in the range of 400–650° F., used to absorb components heavier than propane enters the absorber **19** through line **21**. Overhead dry gas from the absorber is sent to a high pressure amine unit through line **20** where the H_2S is absorbed in an aqueous diethanolamine solution. Bottoms from the absorber **19** exit through line **22** and are commingled in line **24** with the liquid in line **23** from the flash drum **17**. The commingled liquid in line **24** is heated in heat exchanger **25** and enters fractionation tower **27** through line **26**. In the fractionation tower **27** an overhead product boiling between the approximate temperatures of 85° F.–400° F. can be taken off through line **28** and sent to a gasoline stabilizer column for vapor pressure control. A sidestream fraction boiling between the approximate temperatures of 400° F.–650° F. can be diverted through line **29** to the absorber as lean oil or as a No. 2 fuel oil component. The bottoms of fractionation tower **27** leave through line **30**, entering heat exchanger **31** where further heat is supplied. Effluent from exchanger **31** leaves through line **32**, entering a vacuum tower **33**, where a fraction boiling between approximately 650° F.–950° F. can be taken overhead through line **34** to a fluid catalytic cracking unit. Bottoms from vacuum tower **33** leave through line **35** and can be used as a residual fuel blending component.

The following examples are included to illustrate the effectiveness of the instant process for the two-stage hydrogenation of reduced crude without, however, limiting the same.

A 44.7% reduced crude from Tia Juana crude oil feedstock was processed in a number of runs under the conditions set forth in Table I in accordance with the first stage of the instant process. Both catalytic and thermal first stage hydrogenating runs were made. A catalyst containing about 3% Ni, and 14% MoO_3 supported on low grade alumina was used.

TABLE I.—TWO STAGE HYDROGENATION OF REDUCED CRUDE

[First stage]

	Feed	Type Processing—Catalytic							Thermal	
		Catalyst or Inert—Co-Mo on Silica Alumina Support							Extruded Alumina	Tabular Alumina
		Run Number								
		1	2	3	4	5	6	7	8	9
Processing Conditions:										
WHSV, #Oil/Hr./#Catalyst		2.0	1.0	1.0	0.5	1.0	0.5	0.5	0.5	0.5
Pressure, p.s.i.g.		1,500	1,500	1,500	1,500	500	500	500	500	500
Temperature, ° F.		750	750	825	825	750	750	800	750	825
Hydrogen Rate, s.c.f./b		5,000	5,000	5,000	5,000	5,000	5,000	5,000	5,000	5,000
Inspection Tests:										
Gravity, API	16.0	18.8	19.7	24.7	28.2	18.6	19.4	24.2	18.1	19.7
Sulfur Content, wt. percent	2.08	1.17	0.95	0.608	0.317	1.36	1.07	0.682	2.00	1.75
Hydrogen Content, wt. percent	11.51	11.86	12.04	12.30	12.46	11.76	11.83	11.99	11.53	11.75
Carbon Residue, wt. percent	8.95	8.25	7.77	5.61	3.36	8.88	8.02	5.81	8.00	5.35
Pentane Insolubles, wt. percent	8.136	6.327	5.771	4.309	2.243	6.548	6.308	4.155	6.05	5.82
Metals Content:										
NiO, p.p.m.	28.4	17.6	16.4	9.5	3.7	16.4	20.5	10.5	20.6	22.5
V_2O_5, p.p.m.	390	180	200	114	28.5	200	170	43.0	90	105
Hydrogen Consumption, s.c.f./b		294	425	617	740	215	281	414	25	178

The second-stage processing of the treated feedstock is illustrated in Table II for both hydrogenative hydrocracking and hydrogenation of a typical first-stage product. A catalyst containing about 3% Co and 10% MoO_3 was used.

TABLE II.—TWO STAGE HYDROGENATION OF REDUCED CRUDE

[Second stage processing]

Operation	Feedstock	Hydrogenative Hydrocracking	Hydrogenation
Processing Conditions:			
WHSV, #Oil/Hr./#Catalyst		1.0	1.8
Pressure, p.s.i.g.		1500	500
Temperature, ° F.		820	750
Hydrogen Rate, s.c.f./b		2500	5000
Yield Data, wt. percent:			
Hydrogen		−1.24	−0.23
Hydrogen Sulfide		1.85	1.41
Ammonia		0.13	0.02
Methane		0.60	0.17
Ethane		0.49	0.16
Propane		0.54	0.12
Butanes		0.41	0.04
C_5–180° F.		1.84	0.12
180–370° F.		6.20	0.30
370–650° F.	3.2	22.86	5.36
650–950° F.	40.5	40.39	61.72
950° F.+	56.3	25.86	30.75
Carbon		0.07	0.06
Total	100.0	100.00	100.00
Hydrogen Consumption, s.c.f./b		775	145
	Feed		
Inspection Tests—Total Liquid Product:			
Gravity, ° API	19.9	27.5	21.9
Sulfur Content, wt. percent	1.00	0.17	0.82
Hydrogen Content, wt. percent	11.83	12.86	11.94
Nitrogen Content, wt. percent	0.24	0.14	0.20
Carbon Residue, wt. percent	6.51	2.10	5.49
Pentane Insolubles, wt. percent	5.63		
Metals Content:			
NiO, p.p.m.	10.3	2.0	3.0
V_2O_5, p.p.m.	39.0	1.4	8.7
C_5–180° F.: Gravity, ° API		78.6	
180–370° F.:			
Gravity, ° API		51.9	51.2
Sulfur, wt. percent		0.01	0.02
Aromatics, vol. percent		17.4	
Olefins, vol. percent		0.8	
370–650° F.:			
Gravity, ° API		30.7	29.5
Sulfur, wt. percent		0.02	0.48
Carbon Residue, wt. percent		0.01	0.01
ASTM Distillation:			
IBP/10		350/430	427/495
50/90		473/610	580/618

TABLE II—Continued

Operation	Feedstock	Hydrogenative Hydrocracking	Hydrogenation
650–950° F.:			
Gravity, ° API	22.9	26.0	24.1
Sulfur Content, wt. percent	0.50	0.08	0.62
Nitrogen Content, wt. percent		0.12	0.15
Hydrogen Content, wt. percent	12.31	12.64	12.40
Carbon Residue, wt. percent	0.10	0.05	0.12
ASTM Distillation:			
IBP/10		683/739	681/719
30/50		767/812	754/804
70/90		854/905	856/900
95		928	948
950° F.+:			
Gravity, ° API	17.2	19.1	17.2
Sulfur Content, wt. percent	1.40	0.50	1.34
Carbon Residue, wt. percent	11.50	9.90	
KV/210° F., cs	1,190	460	

We claim:

1. A process of two-stage hydrogenation of a reduced mineral oil crude having a substantial asphaltene content comprising hydrogen pretreating said reduced crude over a contact material selected from the group consisting of inert particulate contact materials and Group VIII iron transition series metal promoted hydrogenation catalysts at a temperature of about 600 to 900° F. to agglomerate the asphaltenes present, removing the agglomerated asphaltenes and contact material from the pretreated product in the absence of a solvent and thereafter hydrogen treating the pretreated, deasphalted product in a second stage over a hydrogenation catalyst at a temperature of about 700 to 950° F., a pressure of from about 100 to 2500 p.s.i.g., WHSV of from about 0.3 to 5 pounds reduced crude per hour per pound of material, and hydrogen rate of from about 1000 to 10,000 s.c.f./b.

2. The process of claim 1 wherein the hydrogen pretreating is carried out over an inert particulate contact material.

3. The process of claim 1 wherein said hydrogen pretreating is carried out over a Group VIII iron transition series metal promoted hydrogenation catalyst.

4. The process of claim 3 wherein said catalyst is a cobalt-molybdenum on alumina catalyst.

5. The process of claim 1 wherein improved catalytic cracking feedstocks are produced, said reduced crude being hydrogen treated over said second stage catalyst at a pres-

sure of from about 500 to 2500 p.s.i.g., WHSV of from about 0.3 to 5 lbs. reduced crude/hr./lb. catalyst, temperature of from about 700° to 800° F., and hydrogen rate of from about 1000 to 10,000 s.c f./b.

6. The process of claim 1 wherein hydrocracking occurs, said reduced crude being hydrogen treated over said second-stage catalyst at a pressure of from about 500 to 2500 p.s.i.g., WHSV of from about 0.3 to 2 lbs./hr./lb. catalyst, temperature of from about 750 to 950° F., and hydrogen rate of from about 1000 to 10,000 s.c.f./b.

7. The process of claim 1 wherein said removal comprises filtering the reduced crude following the hydrogen retreating to remove the agglomerated asphaltenes.

8. The process of claim 1 wherein said removal comprises distilling the reduced crude following the hydrogen pretreating and separating the material boiling above about 1100° F., including the asphaltenes and residue, from the lower boiling material.

9. A process for two-stage hydrogenation of a reduced mineral oil crude containing at least about 4% pentane insolubles comprising hydrogen pretreating said reduced crude over a contact material selected from the group consisting of inert particulate contact materials and Group VIII iron transition series metal promoted hydrogenation catalysts at a temperature of about 750 to 850° F., a pressure of about 500 to 1500 p.s.i.g., WHSV of about 0.5 to 2 lbs. crude/hr./lb. material, and hydrogen rate of about 2500 to 5000 s.c.f./b. to agglomerate the asphaltenes present, separating the agglomerated material including asphaltenes and contact material from the pretreated product in the absence of a solvent to produce a pretreated crude having a pentane insolubles content at least 25% less than the original crude, and thereafter hydrogen treating the pretreated, deasphalted crude in a second stage over a hydrogenation catalyst at a temperature of about 700 to 950° F.

10. The process of claim 9 wherein said reduced crude is hydrogen pretreated over an inert particulate contact material.

11. The process of claim 9 wherein improved catalytic cracking feedstocks are produced, said reduced crude being hydrogen treated over said second-stage catalyst at a pressure of from about 500 to 2500 p.s.i.g., WSHV of from about 0.3 to 5 lbs. crude/hr./lb. catalyst temperature of from about 700 to 800° F., and hydrogen rate of from about 1000 to 10,000 s.c.f./b.

12. The process of claim 9 wherein said second stage comprises hydrocracking, said reduced crude is hydrogen treated over said second-stage catalyst at a pressure of from about 500 to 2500 p.s.i.g., WHSV of from about 0.3 to 2 lbs. crude/hr./lb. catalyst, temperature of from about 750 to 950° F., and hydrogen rate of from about 1000 to 10,000 s.c.f./b.

13. A process of two-stage hydrogenaiton of a reduced mineral oil crude containing at least about 4% pentane insolubles comprising hydrogen pretreating said reduced crude over a contact material selected from the group consisting of inert particulate contact materials and Group VIII iron transition series metal promoted hydrogenation catalysts at a temperature of about 750 to 850° F., a pressure of about 500 to 1500 p.s.i.g., WHSV of about 0.5 to 2 lbs. crude/hr./lb. material, and hydrogen rate of about 2500 to 5000 s.c.f./b. to agglomerate the asphaltenes present, filtering the reduced crude following the hydrogen pretreating to remove the agglomerated material, including asphaltenes and contact material from the pretreated product in the absence of a solvent to produce a pretreated crude having a pentane insolubles content at least 25% less than the original crude, and thereafter hydrogen treating the pretreated, deasphalted product in a second stage over a hydrogenation catalyst at a temperature of about 700 to 950° F.

14. A process for two-stage hydrogenation of a reduced mineral oil crude containing at least about 4% pentane insolubles comprising hydrogen pretreating said reduced crude over a contact material selected from the group consisting of inert particulate contact materials and Group VIII iron transition series metal promoted hydrogenation catalysts at a temperature of about 750 to 850° F., a pressure of about 500 to 1500 p.s.i g., WHSV of about 0.5 to 2 lbs. crude/hr./lb. material, and hydrogen rate of about 2500 to 5000 s.c.f./b. to agglomerate the asphaltenes present, distilling the reduced crude following the hydrogen pretreating, separating the material boiling above about 1100° F. including the asphaltenes and residue from the lower boiling material in the absence of a solvent to produce a pretreated crude having a pentane insolubles content at least 25% less than the original crude, and thereafter hydrogen treating the pretreated, deasphalted crude in a second stage over a hydrogenation catalyst at a temperature of about 700 to 950° F.

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