INTEGRATED PROCESS FOR CATALYTIC DEWAXING

FIELD OF THE INVENTION

[0001] This invention related to an integrated catalytic hydrodewaxing process for hydrocarbon feeds. More particularly, a feedstock containing sulfur and nitrogen contaminants is subject to a process including hydrotreating, hydrodewaxing and/or hydrofinishing without disengagement between the process steps.

BACKGROUND OF THE INVENTION

[0002] Dewaxing of hydrocarbon feedstocks is conventionally used to improve the flow properties of the feed, typically by lowering the pour point. Dewaxing catalysts remove waxy components of feeds by either selective hydrocracking or isomerization. The selectivity of dewaxing catalysts may be improved by employing constrained intermediate pore molecular sieves. The activity of such selective catalysts may be improved by employing a metal hydrogenation/dehydrogenation component.

[0003] One problem encountered with dewaxing catalysts is that they are sensitive to environments containing sulfur and/or nitrogen contaminants. Such contaminants negatively impact catalyst activity, catalyst aging and catalyst selectivity. Thus it is common to employ a hydrotreating and/or hydrocracking step prior to the dewaxing step to convert nitrogen and sulfur containing contaminants to ammonia and hydrogen sulfide and to remove these gaseous contaminants from the process prior to the dewaxing step.

[0004] The disadvantage of processes involving separate dewaxing and hydrofinishing steps is that considerable capital investment is involved in the

equipment for these steps. Processes which are directed to lubricants with high VI and low pour points and which combine hydrotreating with conventional dewaxing catalysts such as ZSM-5 run a substantial yield debit since the hydrotreating step is run at more severe conditions in order to compensate for VI loss during hydrodewaxing. More recent dewaxing catalysts which function by isomerization typically require clean feeds, i.e., feeds with very low concentrations of sulfur and nitrogen contaminants. When combined with a pre-hydrotreating step, separation and stripping of gaseous contaminants are normally required to protect catalyst activity.

[0005] It would be desirable to have an integrated process using dewaxing catalysts which are capable of operating in environments containing substantial concentrations of sulfur- and or nitrogen-containing contaminants while maintaining catalyst properties such as selectivity, activity and aging which process functions without the need for a disengagement step to remove gaseous sulfur- and nitrogen containing contaminants.

SUMMARY OF THE INVENTION

[0006] The present invention relates to an integrated dewaxing process capable of operating with highly contaminated feedstocks. The integrated process for dewaxing a raffinate feedstock containing up to 20,000 ppmw sulfur and up to 1000 ppmw nitrogen comprises: (a) contacting the feedstock with a hydrotreating catalyst under hydrotreating conditions to produce a hydrotreated feedstock and gaseous nitrogen- and sulfur-containing contaminants, and (b) passing at least a portion of the hydrotreated feedstock and gaseous components from step (a) without disengagement to a hydrodewaxing zone containing a dewaxing catalyst

including at least one of ZSM-48, ZSM-22, ZSM-23, ZSM-5, ZSM-35, Beta, SSZ-31,SAPO-11, SAPO-31, SAPO-41, MAPO-11, ECR-42, synthetic ferrierites, mordenite, offretite, erionite, and chabazite and hydrodewaxing the hydrotreated feedstock under hydrodewaxing conditions, said dewaxing catalyst including a metal hydrogenation component which is at least one Group 6 metal, at least one Group 8-10 metal, or mixtures of Group 6 and Group 8-10 metals, to form a hydrodewaxed product. As used herein, ZSM-48 includes EU-2, EU-11 and ZBM-20 which are structurally equivalent to ZSM-48.

[0007] Another embodiment relates to an integrated process for dewaxing a raffinate feedstock containing up to 20,000 ppmw sulfur and up to 1000 ppmw nitrogen which comprises: (a) contacting the feedstock with a hydrotreating catalyst under hydrotreating conditions to produce a hydrotreated feedstock and gaseous nitrogen- and sulfur-containing contaminants, (b) passing at least a portion of the hydrotreated feedstock and gaseous sulfur- and nitrogen-containing contaminants from step (a) without disengagement to a hydrodewaxing zone containing a dewaxing catalyst including at least one of ZSM-48, ZSM-22, ZSM-23, ZSM-5, ZSM-35, Beta, SSZ- 31,SAPO-11, SAPO-31, SAPO-41, MAPO-11, ECR-42, synthetic ferrierites, mordenite, offretite, erionite, and chabazite and hydrodewaxing the hydrotreated feedstock under hydrodewaxing conditions, said dewaxing catalyst including a metal hydrogenation component which is at least one Group 6 metal, at least one Group 8-10 metal, or mixtures of Group 6 and Group 8-10 metals, said hydrodewaxing zone also containing a second dewaxing catalyst wherein the second dewaxing catalyst is tolerant of the sulfur- and nitrogen containing contaminants.

[0008] Yet another embodiment relates to an integrated process for dewaxing a raffinate feedstock containing up to 20,000 ppmw sulfur and up to 1000 ppmw nitrogen which comprises: (a) contacting the feedstock with a dewaxing catalyst including at least one of ZSM-48, ZSM-22, ZSM-23, ZSM-5, ZSM-35, Beta, SSZ-31,SAPO-11, SAPO-31, SAPO-41, MAPO-11, ECR-42, synthetic ferrierites, mordenite, offretite, erionite, and chabazite under hydrodewaxing conditions, said dewaxing catalyst including a metal hydrogenation component which is at least one Group 6 metal, at least one Group 8-10 metal, or mixtures of Group 6 and Group 8-10 metals, to form a hydrodewaxed product, and (b) passing at least a portion of the hydrodewaxed product and gaseous components from step (b) to a hydrofinishing zone and hydrofinishing the hydrodewaxed product under hydrofinishing conditions.

[0009] A still further embodiment relates to an integrated process for dewaxing a raffinate feed which comprises: (a) solvent dewaxing the raffinate to form a raffinate and a slack wax, (b) deoiling the slack wax to produce a foots oil, (c) contacting the foots oil with a hydrotreating catalyst under hydrotreating conditions to produce a hydrotreated foots oil and gaseous nitrogen- and sulfur-containing contaminants and (d) passing at least a portion of the hydrotreated foots oil and gaseous sulfur- and nitrogen-containing contaminants from step (c) without disengagement to a hydrodewaxing zone containing a dewaxing catalyst including at least one of ZSM-48, ZSM-22, ZSM-23, ZSM-5, ZSM-35, Beta, SSZ-31,SAPO-11, SAPO-31, SAPO-41, MAPO-11, ECR-42, synthetic ferrierites, mordenite, offretite, erionite, and chabazite and hydrodewaxing the hydrotreated foots oil under hydrodewaxing conditions, said dewaxing catalyst including a metal hydrogenation component which is at least one Group 6 metal, at least one Group

8-10 metal, or mixtures of Group 6 and Group 8-10 metals to from a hydrodewaxed product.

[0010] Another embodiment relates to an integrated process for dewaxing a feedstock containing up to 20,000 ppmw sulfur and up to 1000 ppmw nitrogen comprises: (a) blending a raffinate feedstock and at least one of a slack wax or foots oil to form a blended feedstock, (b) contacting the blended feedstock with a hydrotreating catalyst under hydrotreating conditions to produce a hydrotreated feedstock and gaseous nitrogen- and sulfur-containing contaminants, and (c) passing at least a portion of the hydrotreated feedstock and gaseous components from step (b) without disengagement to a hydrodewaxing zone containing a dewaxing catalyst including at least one of ZSM-48, ZSM-22, ZSM-23, ZSM-5, ZSM-35, Beta, SSZ- 31,SAPO-11, SAPO-31, SAPO-41, MAPO-11, ECR-42, synthetic ferrierites, mordenite, offretite, erionite, and chabazite and hydrodewaxing the hydrotreated feedstock under hydrodewaxing conditions, said dewaxing catalyst including a metal hydrogenation component which is at least one Group 6 metal, at least one Group 8-10 metal, or mixtures of Group 6 and Group 8-10 metals, to form a hydrodewaxed product.

DESCRIPTION OF THE DRAWINGS

[0011] Figure 1 is a graph showing average reactor temperature at given pour point .

[0012] Figure 2 is a graph showing polar tolerance of the catalyst.

[0013] Figure 3 is a graph showing lube yields for dewaxing a medium neutral foots oil over a Crosfield hydrotreating catalyst followed by a Pt/ZSM-48 dewaxing catalyst.

[0014] Figure 4 is a graph showing viscosity of the dewaxed medium neutral foots oil.

[0015] Figure 5 is a graph showing VI of the dewaxed medium neutral foots oil.

[0016] Figure 6 is a graph showing cloud points of the dewaxed medium neutral foots oil.

DETAILED DESCRIPTION OF THE INVENTION

[0017] In the present process, the steps are integrated, i.e., a process that incorporates a sequence of steps which are interrelated and dependent on either earlier or later steps, said steps occurring without disengagement between the sequence of steps.

[0018] Dewaxing catalysts which are isomerization catalysts are normally shape selective intermediate pore molecular sieves loaded with a hydrogenation metal, particularly noble metals. However, such isomerization dewaxing catalysts are considered susceptible to poisoning by sulfur- and nitrogen-containing contaminants such as NH_3 and H_2S. They are thus normally protected by a preceding treatment to remove such poisons. An example of such pre-treatment is conversion of sulfur- and nitrogen-containing contaminants to H_2S and NH_3, respectively, by hydrotreatment. However, hydrotreatement is followed by

disengagement to remove (strip) the sulfur- and nitrogen-containing contaminants prior to dewaxing so as not to poison the catalyst.

[0019] Feeds for the present integrated dewaxing process include raffinates. Raffinates are obtained from solvent extraction processes that selectively dissolve the aromatic components in an extract phase while leaving the more paraffinic components in a raffinate phase. Naphthenes are distributed between the extract and raffinate phases. Typical solvents for solvent extraction include phenol, furfural and N-methyl pyrrolidone. By controlling the solvent to oil ratio, extraction temperature and method of contacting feed to be extracted with solvent, one can control the degree of separation between the extract and raffinate phases. The raffinates may be wide cut or narrow cut.

[0020] The raffinates from solvent extraction may be further subject to solvent dewaxing to separate a lube oil fraction and a slack wax. Solvent dewaxing may be accomplished by treating the raffinates with a solvent such as propane, ketones and mixtures of ketones with aromatics such as benzene, toluene and/or xylene and chilling to crystallize and separate wax molecules. The resulting slack wax is then deoiled to separate a foots oil (soft wax) from microcrystalline wax (hard wax). The slack wax or foots oil may be blended with a raffinate to form a blended feedstock. The ratio of raffinate to slack wax or foots oil in the blended feedstock may range from 99:1 to 1:99.

[0021] The raffinate, slack wax or foots oil feeds are characterized in that they may contain high levels up to 20,000 ppmw of sulfur containing contaminants and up to 1,000 ppmw of nitrogen containing contaminants.

[0022] An important purpose of hydrotreating is to reduce the sulfur and nitrogen content of a feed. Hydrotreating for the present process is not primarily concerned with boiling point conversion of the feed. Hydrotreating catalysts usually contain at least one of Group 6 and Group 8-10 metal (Groups based on the IUPAC Periodic Table format having groups from 1 to 18), on a less acidic support such as alumina or silica. Catalysts may also be bulk metal catalysts wherein the amount of metal may be 30 wt.% or more. Examples include Ni/Mo, Co/Mo and Ni/W catalysts. Preferred hydrotreating catalysts are low acidity, high metals content catalysts such as KF-848 (Akzo Nobel), DN 190 (Criterion catalysts) and RT 721 (Akzo Nobel). The amount of metal is from 0.1 to 95 wt.%, based on catalyst. Hydrotreating conditions include temperatures of 315 - 425°C, pressures of 2170 - 20786 kPa (300 - 3000 psig), liquid hourly space velocities (LHSV) of 0.1 - 10 and hydrogen treat rates of 89 - 1780 m^3/m^3 (500 - 10,000 scf/bbl).

[0023] If a hydrotreating step is used prior to the dewaxing step of the present process, there is no need for disengagement between the hydrotreating and dewaxing step. Disengagement involves depressurization, stripping and repressurization and therefor requires expensive pumps, separators and heaters. This disadvantage is avoided because the present dewaxing catalysts can operate in a sour environment. In the case of raffinates, it may be possible to simply pass the raffinate directly to the dewaxing step without any prior hydrotreatment.

[0024] It has been discovered that certain dewaxing catalysts can function in a sour environment. The present dewaxing catalysts include ZSM-48, ZSM-22, ZSM-23, ZSM-5, ZSM-35, Beta, SSZ- 31,SAPO-11, SAPO-31, SAPO-41, MAPO-11, ECR-42, synthetic ferrierites, mordenite, offretite, erionite, and chabazite, with ZSM-48, ZSM-22, ZSM-5, ZSM-23 and ZSM-35 being preferred while ZSM-48 is

a more preferred embodiment. ZSM-48 is a unidimensional intermediate pore 10 ring zeolite having a pore size of 5.3 Å x 5.6 Å. ZSM-48 is commercially available and its preparation is described in U.S. patents 4,397,827, 4,448,675 and 5,075,269. ZSM-22 is described in U.S. Patent 4,556,477, ZSM-23 in U.S. patent 4,076,342 and ZSM-35 in U.S. patent 4,016,245.

[0025] The dewaxing catalysts are bifunctional, i.e., they are loaded with a metal hydrogenation component, which is at least one Group 6 metal, at least one Group 8 - 10 metal, or mixtures thereof. Preferred metals are Groups 9 -10 metals. Especially preferred are Groups 9 - 10 noble metals such as Pt, Pd or mixtures thereof (based on the IUPAC Periodic Table format having Groups from 1 to 18). These metals are loaded at the rate of 0.1 to 30 wt.%, based on catalyst. Catalyst preparation and metal loading methods are described for example in U.S. Patent No. 6,294,077, and include for example ion exchange and impregnation using decomposable metal salts. Metal dispersion techniques and catalyst particle size control are described in U.S. Patent No. 5,282,958. Catalysts with small particle size and well-dispersed metal are preferred.

[0026] The dewaxing catalysts are typically composited with binder materials which are resistant to high temperatures which may be employed under dewaxing conditions to form a finished dewaxing catalyst or may be binderless (self-bound). The binder materials are usually inorganic oxides such as silica, alumina, silica-aluminas, binary combinations of silicas with other metal oxides such as titania, magnesia, thoria, zirconia and the like and tertiary combinations of these oxides such as silica-alumina -thoria and silica-alumina magnesia. The amount of molecular sieve in the finished dewaxing catalyst is from 10 to 100, preferably 35 to 100 wt.%, based on catalyst. Such catalysts are formed by methods such spray

drying, extrusion and the like. The dewaxing catalyst may be used in the sulfided or unsulfided form, and is preferably in the sulfided form.

[0027] The temperature for the present dewaxing process is in the range from 360 to 425°C . Due to the catalyst structure, these temperatures may be higher than the temperatures normally used for catalytic dewaxing without the cracking that might otherwise be expected from such higher temperatures. Other process conditions include hydrogen pressures of from 2859 - 20786 kPa (400 to 3000 psig), liquid hourly space velocities of 0.1 to 10 LHSV and hydrogen treat gas rates of from 53.4 - 1780 m^3/m^3 (300 to 10,000 scf/bbl).

[0028] The hydrodewaxing catalyst may contain a second catalytic component which may be admixed with the ZSM-48 dewaxing catalyst or may be in a stacked (layered) configuration with the second component in the upper layer. The second catalyst is tolerant of sulfur- and nitrogen-containing contaminants. Typical catalysts that are tolerant of such contaminants include ZSM-5 and larger pore catalysts such as zeolite beta. A convenient measure of the extent to which a dewaxing catalyst provides control molecules of varying sizes to its internal structure is the Constraint Index of the zeolite. Zeolites which provide a highly restricted access to and egress from its internal structure have a high value for the Constraint Index, and zeolites of this kind usually have pores of small size. On the other hand, zeolites which provide relatively free access to the internal zeolite structure have a low value for the Constraint Index. The method by which Constraint Index is determined is described fully in U.S. Pat. No.4,016,218, to which reference is made for details of the method. Large pore zeolites having Constraint Indices less than 1 include TEA mordenite (0.4), dealuminized Y (0.5), ZSM-4 (0.5), ZSM-20 (0.5), mordenite (0.5), REY (0.4) and ultrastable Y. Zeolite

beta is also within the scope of large pore zeolites. The second catalytic component may also be acidic porous amorphous materials, such as amorphous aluminosilicate, halogenated alumina, acidic clay, alumina or silica-alumina.

[0029] At least a portion of the products from the hydrodewaxing zone or step may then be passed to a hydrofinishing step again without the need of disengagement between the hydrodewaxing and hydrofinishing steps. Catalysts for hydrofinishing can the same as those used for the preliminary hydrotreating step, if any, i.e., those containing at least one of Group 6 and Group 8-10 metal on a support such as alumina or silica. Examples include Ni/Mo, Co/Mo and Ni/W catalysts. Preferred hydrotreating catalysts include catalyst such as KF-840, KF-848 (Akzo Nobel), DN 190 (Criterion catalysts) and RT 721 (Akzo Nobel).

[0030] The hydrofinishing catalyst may also be a crystalline mesoporous material belonging to the M41S class or family of catalysts. The M41S family of catalysts are crystalline mesoporous materials having high silica contents whose preparation is further described in J. Amer. Chem. Soc., 1992, 114, 10834. Examples included MCM-41, MCM-48 and MCM-50. A preferred member of this class is MCM-41 whose preparation is described in US Patent No. 5,098,684. MCM-41 is characterized by having a hexagonal crystal structure with a unidimensional arrangement of pores having a cell diameter greater than 13 Angstroms. The physical structure of MCM-41 is like a bundle of straws wherein the opening of the straws (the cell diameter of the pores) ranges from 13 to 100+ Angstroms. MCM-48 has a cubic symmetry and is described for example is U.S. Patent No. 5,198,203 whereas MCM-50 has a lamellar structure and is described in US Patent No. 5,246,689.

[0031] The amount of metal is from 0.1 to 5 wt.%, preferably 0.2 to 2 wt.%, based on catalyst. Hydrofinishing conditions include temperatures of 150 -350°C, preferably 180 - 300°C, pressures of 100 - 3000 psig (790 - 20786 kPa), preferably 50 - 2500 psig (1135 - 17339 kPa), LHSV of 0.1 - 20, preferably 0.2 - 15 and treat gas rates of 300 - 10000 scf/bbl (53 - 1780 m^3/m^3), preferably 450 -5000 scf/B (80 - 890 m^3/m^3).

[0032] If the raffinate feed is passed directly to hydrodewaxing without a preliminary hydrotreating step, then dewaxed product from hydrodewaxing is passed to hydrofinishing without disengagement. The preferred hydrofinishing conditions will include a temperature range of from 150 - 300°C.

[0033] The product from the hydrofinishing step is typically passed to a separator which may include stripping and /or fractionation. In the separation zone, sulfur- and nitrogen containing contaminants, especially hydrogen sulfide and ammonia, are separated together with other gaseous components from liquid product. The liquid product may be fractionated to obtain various cuts of lubricating oil products based on boiling range.

[0034] The process sequence may include the following steps in various combinations. A waxy feed is first solvent extracted to separate a raffinate and an extract. The raffinate may then be sent directly to hydrotreating, may be hydrodewaxed directly or may be solvent dewaxed to produce a lubricating oil and a slack wax. Upon deoiling, the slack wax yields a hard wax and foots oil which may then be sent to hydrotreating.

[0035] In the sequence raffinate to hydrotreating to hydrodewaxing and optionally hydrofinishing, there is no disengagement between any of the process sequence steps. The hydrotreating and hydrodewaxing steps may take place sequentially in separate reactors or may occur as stacked beds in a single reactor. Any hydrofinishing step will occur in a separate reactor. If the hydrodewaxing step involves more than one dewaxing catalyst, then the hydrodewaxing step may involve a mixture of dewaxing catalysts in a single reactor, stacked beds in a single reactor, or separate reactors in sequence each containing a dewaxing catalyst.

[0036] The process sequence involving foots oils may include hydrotreating, hydrodewaxing and optionally hydrotreating. As in the case of raffinates, the sequence may take place sequentially in separate reactors or may occur as stacked beds in a single reactor.

[0037] The invention is further illustrated by the following examples which are not intended as limiting.

EXAMPLES

Example 1

[0038] Table 1compares three processing configurations for dewaxing a 260 Neutral raffinate containing 6680 wppm sulphur and 50.6 wppm nitrogen and a dry wax content of 16.75 wt.% on feed at -18 pour point. Column A illustrates the properties of a dewaxed oil obtained by solvent dewaxing with methylisobutyl ketone at a feed to solvent ratio of 3:1, the 260 Neutral raffinate. Prior to solvent dewaxing, the raffinate had been hydrotreated over an Akzo KF-848 hydrotreated

catalyst at an average reactor temperature of 350°C, 0.53 LHSV, at a treat gas rate of 2600 SCF H_2/bbl of feed and 1800psig. The sulphur and nitrogen contents of the hydrotreated raffinate were less than 2 wppm.

Table 1

	A	B	C
Process	**Hydrotreating + Solvent Dewaxing**	**Hydrotreating + depressurization + hydrodewaxing**	**Untreated feed + hydrodewaxing**
HDW Average Reactor Temperature, °C	n/a	310	370
Yield of 370°C+ DWO on Raw Feed, wt%	61.2	70.2	65.1
Dewaxed Oil Properties			
Viscosity, cSt at 100°C	6.1	5.6	5.4
Viscosity, cSt at 40°C	36.8	31.4	29.7
Viscosity Index	113	120	117
Pour Point,°C	-17	-17	-16
Cloud Point, °C	-14	-6	-13
Cloud -Pour Spread, °C	3	11	3

[0039] Column B illustrates the properties of the product made by hydrotreating the 260N raffinate over Akzo KF 848 at an average reactor temperature of 350°C, 0.53LHSV, 1800psig and at a treat gas rate of 2600SCF H_2/bll of feed but followed by catalytic dewaxing over a hydrodewaxing catalyst containing ZSM-48. The process conditions during hydrodewaxing were 0.76 LHSV, 1650SCF/B H_2, and 1800psig. In this example the gas phase polar species (e.g., ammonia and hydrogen

sulphide) were removed before the hydrodewaxing step. Comparing the products in columns A and B it can be seen that the yield and VI of product after hydrodewaxing in increased over that obtained by solvent dewaxing at constant pour point. One other item to note is that the cloud - pour spread of the hydrodewaxed product is considerably larger than that of the solvent dewaxed product.

[0040] Column C illustrates the properties of the product made by hydrotreating the 260N raffinate over Akzo KF 848 at an average reactor temperature of 350°C, 0.53LHSV and at a treat gas rate of 2600SCF H_2/bbl of feed but hydrodewaxing over a hydrodewaxing catalyst containing ZSM-48. The process conditions in the hydrodewaxing stage were 0.76 LHSV, 1650SCF/B H_2, and 1800psig. In this illustration, the gas phase polar species generated during the hydrotreating stage, were cascaded with the hydrogen over the hydrodewaxing stage which required that the temperature of the dewaxing stage was higher than that in column B. Comparing the products in columns A and B with the product in column C, it can be seen that the yield and VI of product after hydrodewaxing in increased over that obtained by solvent dewaxing. It is noted that the cloud - pour spread of the hydrodewaxed product made at elevated reactor temperature in a sour gas environment is similar to that of the solvent dewaxed product.

Example 2

[0041] Table 2 compares three processing configurations for dewaxing a 130 Neutral raffinate containing 2500wppm sulphur and 25 wppm nitrogen and a dry wax content of 16.44 wt.% on feed at -16°C pourpoint. Column A illustrates the properties of a dewaxed oil obtained by solvent dewaxing with methylisobutyl

ketone at a feed to solvent ratio of 3:1, the 130 Neutral raffinate. Prior to solvent dewaxing, the raffinate had been hydrotreated over an Akzo KF848 hydrotreated catalyst at an average reactor temperature of 350°C, 0.53LHSV, at a treat gas rate of 2600SCF H_2/bll of feed and 1800psig. The sulphur and nitrogen contents of the hydrotreated raffinate were less than 2wppm.

Table 2

	A	B	C
Process	**Hydrotreating + Solvent Dewaxing**	**Hydrotreating + depressurization + hydrodewaxing**	**Untreated feed + hydrodewaxing**
HDW Average Reactor Temperature, °C	n/a	310	370
Yield of 370°C+ DWO on Raw Feed, wt%	57.12	57.6	44.23
Dewaxed Oil Properties			
Viscosity, cSt at 100°C	4.28	4.04	3.654
Viscosity, cSt at 40°C	20.752	18.352	15.823
Viscosity Index	112	120	116
Pour Point,°C	-27	-27	-26
Cloud Point, °C	-28	-17	-24
Cloud -Pour spread,°C	-	10	2

[0042] Column B illustrates the properties of the product made by hydrotreating the 130N raffinate over Akzo KF 848 at an average reactor temperature of 350°C, 0.53LHSV, 1800psig and at a treat gas rate of 2600SCF H_2/bll of feed but followed by catalytic dewaxing over a hydrodewaxing catalyst containing ZSM-48. The

process conditions during hydrodewaxing were 0.76 LHSV, 1650SCF/B H_2, and 1800psig. In this example the gas phase polar species (e.g., ammonia and hydrogen sulphide) were removed before the hydrodewaxing step. Comparing the products in columns A and B it can be seen that the yield and VI of product after hydrodewaxing in increased over that obtained by solvent dewaxing at constant pour point. One other item to note is that the cloud - pour spread of the hydrodewaxed product is considerably larger than that of the solvent dewaxed product.

[0043] Column C illustrates the properties of the product made by hydrotreating the 130N raffinate over Akzo KF 848 at an average reactor temperature of 350°C, 0.53LHSV and at a treat gas rate of 2600SCF H_2/bll of feed but hydrodewaxing over a hydrodewaxing catalyst containing ZSM-48. The process conditions in the hydrodewaxing stage were 0.76 LHSV, 1650SCF/B H_2, and 1800psig. In this illustration, the gas phase polar species generated during the hydrotreating stage, were cascaded with the hydrogen over the hydrodewaxing stage which required that the temperature of the dewaxing stage was higher than that in column B. Comparing the products in columns A and B with the product in column C, it can be seen that the yield and VI of product after hydrodewaxing increased over that obtained by solvent dewaxing at the same pour point. It is noted that the cloud - pour spread of the hydrodewaxed product made at elevated reactor temperature in a sour gas environment, column C, is similar to that of the solvent dewaxed product.

Example 3

[0044] This example illustrates the effect of treat gas rate on the hydrodewaxing stage operating in a sour gas environment. The 130N raffinate was hydrotreated

over Akzo KF 848 at an average reactor temperature of 350°C, 0.53LHSV and at a treat gas rate of 2600SCF H_2/bll of feed and hydrodewaxing over a hydrodewaxing catalyst containing ZSM-48. The process conditions in the hydrodewaxing stage were 0.76 LHSV, 1650 to 2500SCF/B H_2, and 1800psig. In this illustration, the gas phase polar species generated during the hydrotreating stage were cascaded with the hydrogen over the hydrodewaxing stage. The hydrodewaxing catalyst is a ZSM-48 bound with alumina (35/65 wt ratio respectively) operating under a series of conditions shown in Figure 1. The figure illustrates that by increasing the treat gas rate from 1650SCFH_2/B feed to 2100 and then to 2500SCFH_2/B feed, the Average Reactor Temperature required to maintain a feed pour point of 10°F decreases from 690 to 680°F for a 130N raffinate.

Example 4

[0045] This example illustrates the application of a hydrodewaxing catalyst catalyst, containing ZSM-48 and alumina 65/35wt%, for hydrodewaxing a 130N waxy raffinate containing , 7270 wppm sulfur and 32.6 wppm of total nitrogen, and a dry wax content of 17wt% on feed at a pour point of -18°Cat 400 psig H_2 and 2500SCF/B H_2 without pre-hydrotreating but having a hydrofinishing step.

[0046] The processing conditions were as listed in Table 3 and the product quality data in Table 4.

Table 3

	LHSV	Pressure Psig	Gas Rate , SCF/B feed	Average Reactor Temperature, °C
Hydrodewaxing	0.5-1.0	400	2500	350 - 380
Hydrofinishing	0.5-1.0	400	2500	290

Table 4

	A	B
Process	**Solvent Dewaxing**	**Untreated feed + hydrodewaxing**
HDW Average Reactor Temperature, °C	n/a	370
Yield of 370°C+ DWO on Raw Feed, wt%	82.9	72.4
Dewaxed Oil Properties		
Viscosity, cSt at 100°C	4.93	4.44
Viscosity, cSt at 40°C	28.45	23.06
Viscosity Index	94	102
Pour Point,°C	-19	-19

[0047] Table 4 illustrates that hydrodewaxing the unhydrotreated waxy raffinate gives a 370°C+ product having an eight point higher VI than that produced by solvent dewaxing.

[0048] Figure 2 illustrates the polar tolerance of the catalyst given 50 days on stream with the unhydrotreated 130N Raffinate feedstock.

Example 5

[0049] This Example illustrates the cascade dewaxing of a foots oil feed. Two soft wax feeds, a medium neutral Foots oil (MNFO) and light neutral Foots oil (LNFO), were used for the dewaxing study. The properties of the feeds are summarized as follows.

Table 5

Properties of Foots Oils

Feed	Medium Neutral Foots Oil	Light Neutral Foots Oil
KV@100°C, cSt	5.513	3.207
KV@40°C, cSt	-	23.84
Pour Point, °C	45	36
Density, g/cc	0.8453	0.8241
N content, ppm	19	< 8
S content, ppm	1851	1807
Aromatics, %	12.1	8.9
Boiling Range, °F	715-950	650-918
Oil Content, %	38.12	33.7

[0050] Two catalysts were employed for dewaxing the Foots oil feeds. Crosfield 599 was used as a pre-hydrotreating catalyst followed by Pt/ZSM-48 dewaxing catalyst. Crosfield 599 is a commercial catalyst containing a mixture of NiO and MoO_3 supported on alumina. The properties and metal contents of the catalyst are shown below.

[0051] Crosfield *599*: 224 m^2/g (surface area), 1.37 g/cc (particle density), 35% Al, 3.8% Ni, 17% Mo.

[0052] The dewaxing catalyst was alumina (35 wt.%) bound, ZSM-48 crystals containing 0.6 wt.% platinum.

[0053] The dewaxing experiments were performed using a microunit equipped with two cascaded down-flow trickle bed tubular reactors and two three-zone furnaces. The unit was heat-traced to avoid freezing of the waxy feedstocks. To reduce feed bypassing and lower zeolite pore diffusion resistance, the catalyst extrudates were crushed and sized to 60-80 mesh. The first reactor was then loaded with a mixture of 7.5 cc of the sized Crosfield 599 and 3 cc of 80-120 mesh sand. The second reactor was loaded with a mixture of 15 cc of the sized Pt/ZSM-48 and 5 cc of 80-120 mesh sand.

[0054] After pressure testing of the unit, the catalysts were dried and reduced at 204°C (400°F) for one hour under 1 atmosphere, 255 cc/min hydrogen flow. The catalysts were then sulfided at 371°C (700°F) for 12 h using 100 cc/min, 2% H_2S in H_2. The MNFO was first processed over the cascaded Crosfield 599/Pt-ZSM-48, followed by switching feed to the LNFO. Isomerization and dewaxing of the Foots oil feeds was conducted under 2860-6996 kPa (400-1000 psig) H_2 at 2.0 h^{-1} LHSV based on Crosfield 599 and 1.0 h^{-1} LHSV based on Pt/ZSM-48. Hydrogen/feed ratio was set at 1015 m^3/m^3 (5700 scf/bbl). The dewaxing experiments were started first by saturating the catalyst beds with feed at 204°C (400°F), then heating the two reactors to initial operating temperature (the two reactors were maintained at same temperature). Material balances were carried out overnight for 16 h after 8 h lineout. Reactors temperature was then gradually changed to vary pour point.

[0055] Off-gas samples were analyzed by GC. Total liquid products (TLPs) were weighed and analyzed by simulated distillation. TLPs were distilled into initial boiling point (IBP) -166°C (-330°F) naphtha, 166-343°C (330-650°F) distillate, and 343°C+ (650°F+) lube fractions. The 343°C+ (650°F+) lube

fractions were again analyzed by simulated distillation (Simdis) to ensure accuracy of the actual distillation operations. The pour point and cloud point of 343°C+ 650°F+ lubes were measured according to corresponding ASTM D97 and D2500 methods, and their viscosities were determined at both 40°C and 100°C according to ASTM D445-3 and D445-5 methods, respectively.

[0056] The dewaxing of the MNFO was carried out under 6996 kPa (1000 psig) H_2 at 2.0 h^{-1} LHSV based on Crosfield 599 and 1.0 h^{-1} LHSV based on Pt/ZSM-48. Hydrogen/feed ratio of 1015 m^3/m^3 (5700 scf/bbl) was used. The temperature of both Reactor 1 (containing Crosfield 599) and Reactor 2 (containing Pt/ZSM-48) was kept same. The dewaxed oil yields and properties are summarized in Table 6. For further clarification, the dewaxing results are also illustrated in Figures 3-6.

Table 6

Lube Yield and Properties for Dewaxing the MNFO under 1000 psig H_2

Temp (°C)	650°F+ Yield, wt% Feed	KV@100°C (cSt)	VI	Pour Point (°C)	Cloud Point (°C)	S (ppm)	N (ppm)	Tot. Arom (mmol/Kg)
354	82	5.364	141.8	18	30	29	< 5	223
360	73	5.224	135.8	9	22	28	< 5	227
363	67	5.342	132.8	6	17	< 25	< 5	230
368	60	5.436	125.8	-3	5	< 25	< 5	249
374	49	5.851	114.6	-27	-18	< 25	< 5	270
379	34	5.727	106.6	< -54	< -54	< 25	< 5	305

[0057] The results show that the cascaded dual catalysts system consisting of first bed Crosfield 599 pre-hydrotreating catalyst followed by second bed Pt/ZSM-

48 dewaxing catalyst is capable of converting the medium neutral Foots oil to high VI (> 120) Group III lube base stocks with low sulfur (< 25 ppm) and nitrogen (< 5 ppm) contents. Lube yield of about 60% was obtained at conventional pour point.

Example 6

[0058] To test the pressure effects on the catalysts performance and lube product properties, the dewaxing of the MNFO was also performed under 2859 kPa (400 psig) H_2. Other conditions, such as LHSV, hydrogen/feed ratio, were similar to those used in the previous process under 6996 kPa (1000 psig) H_2. The temperature of Reactor 1 (containing Crosfield 599) and Reactor 2 (containing Pt/ZSM-48) was kept same. The dewaxed oil yields and properties are summarized in Table 7.

Table 7

Lube Yield and Properties for Dewaxing the MNFO under 400 psig H_2

Temp (°C)	343°C+ Yield, wt% Feed	KV@100°C (cSt)	VI	Pour Point (°C)	Cloud Point (°C)	S (ppm)	N (ppm)	Tot. Arom (mmol/Kg)
354	77.6	5.429	142.0	24	36	-	-	-
360	73.6	5.557	136.4	18	24	-	-	-
363	71.3	5.442	132.2	12	21	-	-	-
366	67.7	5.513	129.2	9	18	-	-	-
368	62.0	5.372	125.0	-3	8	49	< 5	402
371	57.4	5.916	119.3	-6	2	48	< 5	425
374	54.5	5.409	116.3	-24	-5	37	< 5	478
377	50.8	5.933	111.1	-33	-17	-	-	-
379	45.7	5.316	108.4	< -54	-51	-	-	-

[0059] The above results demonstrate that the cascaded dual catalysts system remains effiective for dewaxing Foots oil at hydrogen pressure as low as 2859 kPa

(400 psig). Low pressure process has significant advantages versus high pressure operation because of the simplicity and low cost in design and construction of low pressure reactors. By comparing to the dewaxing data obtained at 6996 kPa (1000 psig) H_2, the hydrogen pressure effects on catalysts activity was found to be minimal for this particular feed with high contents of sulfur and nitrogen. Upon decreasing H_2 pressure, the lube yield is slightly higher at conventional pour point with essentially no change in lube VI. At a low hydrogen pressure, the effectiveness of the pre-hydrotreating catalyst (Crosfield 599) decreases; as the result, both sulfur and aromatic contents in the lube products increase (see Tables 6 and 7).

Example 7

[0060] This example shows the dewaxing of LNFO at 6996 kPa H_2. The process conditions used for dewaxing the LNFO were similar to those for the MNFO. The experiments were carried out under 6996 kPa (1000 psig) H_2 at 2.0 h^{-1} LHSV based on Crosfield 599 and 1.0 h^{-1} LHSV based on Pt/ZSM-48. Hydrogen/feed ratio of 5700 scf/bbl (1015 m^3/m^3) was employed. The temperature of Reactor 1 (containing Crosfield 599) and Reactor 2 (containing Pt/ZSM-48) was kept same. The dewaxed oil yields and properties are summarized in Table 8; and for further clarification, the results are depicted in Figures 5-8.

Table 8

Lube Yield and Properties for Dewaxing the LNFO under 1000 psig H_2

DOS (days)	Temp (°F)	343 °C+ Yield, wt% Feed	KV@100°C (cSt)	VI	Pour Point (°C)	Cloud Point (°C)	S (ppm)
27	650	82.0	3.280	141.0	24	27	< 25
28	660	78.0	3.435	140.0	21	23	-
30	675	67.6	3.458	132.5	9	19	< 25
31	680	61.2	3.530	128.6	3	7	< 25
32	685	57.2	3.464	123.1	-9	-1	< 25
34	695	46.6	4.122	120.9	-33	-10	< 25
42	670	66.6	3.193	130.6	0	5	< 25

[0061] These results demonstrate that the cascaded dual catalysts system is also effective and selective in converting the light neutral Foots oil to high VI (> 120), low sulfur (< 25 ppm) Group III lube base stocks. Lube yield of about 57% was obtained at conventional pour point.

[0062] In addition, the data in Table 8 show that after 10 days on stream upon switching feed from the MNFO to the LNFO, the catalyst activity increases by approximately 10°F, along with small lube yield (+5%) and VI (+2) increase.

Example 8

[0063] Byproduct Yields for Dewaxing the MNFO and LNFO were determined as follows. The processes were carried out under 6996 kPa (1000 psig) H_2 at 2.0 h^{-1} LHSV based on Crosfield 599 and 1.0 h^{-1} LHSV based on Pt/ZSM-48. Hydrogen/feed ratio of 1015 m^3/m^3 (5700 scf/bbl was employed. The temperature

of Reactor 1 (containing Crosfield 599) and Reactor 2 (containing Pt/ZSM-48) was kept same. The yields of dewaxed oil and lighter byproducts are summarized in Table 9. For both MNFO and LNFO dewaxing, the major byproducts were distillate and naphtha with relatively small amount (< 8%) of C_1-C_4 gases.

Table 9

Byproduct Yields (wt% Feed) for Dewaxing the MNFO and LNFO

Feed	Process Temp (°C)	343°C^F+ Lube PP (°C)	343°C+ Lube Yield	166-343°C Distillate Yield	C_5-166°C Naphtha Yield	C_1-C_4 Offgas Yield
MNFO	368	-3	60.0	19.1	17.9	5.1
LNFO	363	-9	57.2	21.8	13.9	6.2
LNFO	368	-33	46.6	26.1	23.2	7.7

CLAIMS:

1. An integrated process for dewaxing a raffinate feedstock containing up to 20,000 ppmw sulfur and up to 1000 ppmw nitrogen which comprises: (a) contacting the feedstock with a hydrotreating catalyst under hydrotreating conditions to produce a hydrotreated feedstock and gaseous nitrogen- and sulfur-containing contaminants, and (b) passing at least a portion of the hydrotreated feedstock and gaseous components from step (a) without disengagement to a hydrodewaxing zone containing a dewaxing catalyst including at least one of ZSM-48, ZSM-22, ZSM-23, ZSM-5, ZSM-35, Beta, SSZ- 31,SAPO-11, SAPO-31, SAPO-41, MAPO-11, ECR-42, synthetic ferrierites, mordenite, offretite, erionite, and chabazite and hydrodewaxing the hydrotreated feedstock under hydrodewaxing conditions, said dewaxing catalyst including a metal hydrogenation component which is at least one Group 6 metal, at least one Group 8-10 metal, or mixtures of Group 6 and Group 8-10 metals, to form a hydrodewaxed product.

2. An integrated process for dewaxing a raffinate feedstock containing up to 20,000 ppmw sulfur and up to 1000 ppmw nitrogen which comprises: (a) contacting the feedstock with a hydrotreating catalyst under hydrotreating conditions to produce a hydrotreated feedstock and gaseous nitrogen- and sulfur-containing contaminants, (b) passing at least a portion of the hydrotreated feedstock and gaseous sulfur- and nitrogen-containing contaminants from step (a) without disengagement to a hydrodewaxing zone containing a dewaxing catalyst including at least one of ZSM-48, ZSM-22, ZSM-23, ZSM-5, ZSM-35, Beta, SSZ-31,SAPO-11, SAPO-31, SAPO-41, MAPO-11, ECR-42, synthetic ferrierites, mordenite, offretite, erionite, and chabazite and hydrodewaxing the hydrotreated feedstock under hydrodewaxing conditions, said dewaxing catalyst including a

metal hydrogenation component which is at least one Group 6 metal, at least one Group 8-10 metal, or mixtures of Group 6 and Group 8-10 metals, said hydrodewaxing zone also containing a second dewaxing catalyst wherein the second dewaxing catalyst is tolerant of the sulfur- and nitrogen-containing contaminants.

3. An integrated process for dewaxing a raffinate feedstock containing up to 20,000 ppmw sulfur and up to 1000 ppmw nitrogen which comprises: (a) contacting the feedstock with a dewaxing catalyst including at least one of ZSM-48, ZSM-22, ZSM-23, ZSM-5, ZSM-35, Beta, SSZ- 31,SAPO-11, SAPO-31, SAPO-41, MAPO-11, ECR-42, synthetic ferrierites, mordenite, offretite, erionite, and chabazite under hydrodewaxing conditions, said dewaxing catalyst including a metal hydrogenation component which is at least one Group 6 metal, at least one Group 8-10 metal, or mixtures of Group 6 and Group 8-10 metals, to form a hydrodewaxed product, and (b) passing at least a portion of the hydrodewaxed product and gaseous components from step (b) to a hydrofinishing zone and hydrofinishing the hydrodewaxed product under hydrofinishing conditions.

4. An integrated process for dewaxing a raffinate feed which comprises: (a) solvent dewaxing the raffinate to form a raffinate and a slack wax, (b) deoiling the slack wax to produce a foots oil, (c) contacting the foots oil with a hydrotreating catalyst under hydrotreating conditions to produce a hydrotreated foots oil and gaseous nitrogen- and sulfur-containing contaminants and (d) passing at least a portion of the hydrotreated foots oil and gaseous sulfur- and nitrogen-containing contaminants from step (c) without disengagement to a hydrodewaxing zone containing a dewaxing catalyst including at least one of ZSM-48, ZSM-22, ZSM-23, ZSM-5, ZSM-35, Beta, SSZ- 31,SAPO-11, SAPO-31, SAPO-41, MAPO-11, ECR-

42, synthetic ferrierites, mordenite, offretite, erionite, and chabazite and hydrodewaxing the hydrotreated foots oil under hydrodewaxing conditions, said dewaxing catalyst including a metal hydrogenation component which is at least one Group 6 metal, at least one Group 8-10 metal, or mixtures of Group 6 and Group 8-10 metals to from a hydrodewaxed product.

5. An integrated process for dewaxing a feedstock containing up to 20,000 ppmw sulfur and up to 1000 ppmw nitrogen comprises: (a) blending a raffinate feedstock and at least one of a slack wax or foots oil to form a blended feedstock, (b) contacting the blended feedstock with a hydrotreating catalyst under hydrotreating conditions to produce a hydrotreated feedstock and gaseous nitrogen- and sulfur-containing contaminants, and (c) passing at least a portion of the hydrotreated feedstock and gaseous components from step (b) without disengagement to a hydrodewaxing zone containing a dewaxing catalyst including at least one of ZSM-48, ZSM-22, ZSM-23, ZSM-5, ZSM-35, Beta, SSZ- 31,SAPO-11, SAPO-31, SAPO-41, MAPO-11, ECR-42, synthetic ferrierites, mordenite, offretite, erionite, and chabazite and hydrodewaxing the hydrotreated feedstock under hydrodewaxing conditions, said dewaxing catalyst including a metal hydrogenation component which is at least one Group 6 metal, at least one Group 8-10 metal, or mixtures of Group 6 and Group 8-10 metals, to form a hydrodewaxed product.

6. An integrated process for dewaxing a raffinate feedstock containing up to 20,000 ppmw sulfur and up to 1000 ppmw nitrogen which comprises: (a) contacting the feedstock with a hydrotreating catalyst under hydrotreating conditions to produce a hydrotreated feedstock and gaseous nitrogen- and sulfur-containing contaminants, and (b) passing at least a portion of the hydrotreated

feedstock and gaseous components from step (a) without disengagement to a hydrodewaxing zone containing a ZSM-48 dewaxing catalyst and hydrodewaxing the hydrotreated feedstock under hydrodewaxing conditions, said dewaxing catalyst including a metal hydrogenation component which is at least one Group 6 metal, at least one Group 8-10 metal, or mixtures of Group 6 and Group 8-10 metals, to form a hydrodewaxed product.

7. The process of any of the preceding claims wherein the hydrotreating conditions temperatures of 315 - 425°C, pressures of 2170 - 20786 kPa, Liquid Hourly Space Velocities (LHSV) of 0.1 - 10 and hydrogen treat rates of 89 - 1780 m^3/m^3.

8. The process of any of the preceding claims wherein the metal hydrogenation component is Pt, Pd or mixtures thereof.

9. The process of any of the preceding claims wherein the hydrodewaxing conditions include a temperature of 360 to 425°C, hydrogen pressures of from 2859 - 20786 kPa, liquid hourly space velocities of 0.1 to 10 LHSV and hydrogen treat gas rates of from 53.4 - 1780 m^3/m^3.

10. The process of claims 1, 2 or 6 further comprising a hydrofinishing step following step (b).

11. The process of claims 4 or 5 further comprising a hydrofinishing step following step (c).

12. The process of claims 1, 2, 3, 4, or 5 wherein the dewaxing catalyst contains ZSM-48.

13. The process of claims 1 or 6 wherein the dewaxing catalyst further comprises a second dewaxing catalyst.

14. The process of claim 2 or 13 wherein the second dewaxing catalyst is ZSM-5 or zeolite beta.

15. The process of any of the preceding claims wherein the hydrofinishing conditions include temperatures of 150 -350°C, pressures of 100 - 3000 psig (790 - 20786 kPa), LHSV of 0.1 - 20, and treat gas rates of 300 - 10000 scf/bbl (53 - 1780 m^3/m^3).