

CATALYTIC DEWAXING PROCESS

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims priority to U.S. Provisional Application Serial No. 61/284,835 filed December 24, 2009, herein incorporated by reference in its entirety.

FIELD

[0002] The present disclosure relates to a process for catalytically dewaxing feeds having a variety of wax contents.

BACKGROUND

[0003] Waxy feedstocks may be used to prepare basestocks having a high viscosity index (VI). However, in order to obtain a basestock having the low temperature properties suitable for most uses, it is usually necessary to dewax the feedstock. Dewaxing may be accomplished by means of a solvent or catalytically. Solvent dewaxing is a physical process whereby waxes are removed by contacting with a solvent, such as methyl ethyl ketone, followed by chilling to crystallize the wax and filtration to remove the wax. Catalytic dewaxing involves chemically converting the less desirable molecules to produce a basestock with more favorable low temperature properties. Long chain normal paraffins and slightly branched paraffins readily solidify and thus result in generally unfavorable low temperature properties. Catalytic dewaxing is a process for converting these long chain normal paraffins and slightly branched paraffins to improve the low temperature properties of the feed.

[0004] Catalytic dewaxing may be accomplished using catalysts that function primarily by cracking waxes to lower boiling products, or by catalysts that

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primarily isomerize waxes to more highly branched products. Catalysts that dewax by cracking decrease the yield of lubricating oils while increasing the yield of lower boiling distillates. Catalysts that isomerize do not normally result in significant boiling point conversion. Catalysts that dewax primarily by cracking are exemplified by the zeolites ZSM-5, ZSM-11, ZSM-12, and offretite. Catalysts that dewax primarily by isomerization are exemplified by the zeolites ZSM-22, ZSM-23, SSZ-32, ZSM-35, and ZSM-48.

[0005] In many refineries it is necessary to be able to dewax feeds having very large differences in wax content varying from, for example, a slack wax containing of the order of 90 wt% wax to a hydrocrackate containing 20 wt% or less wax. In addition, despite the fact that zeolite dewaxing catalysts are generally susceptible to poisoning by sulfur and nitrogen impurities, it is also often necessary to handle feeds with a wide range of impurity levels.

[0006] Currently, the solution adopted by most refineries to deal with the problem of varying wax content is to employ two different dewaxing trains, each having a different dewaxing catalyst. One dewaxing train is then used for low wax content feeds while the other is used for high wax content feeds. Although this is a costly solution, the limited activity of current dewaxing catalysts makes it difficult to design a single plant that can handle all types of feed and still provide an acceptably high throughput in the case of high wax feeds.

[0007] United States Published Patent Application No. 2007/0131581 discloses ZSM-48 having a silica to alumina molar ratio of 110 or less that is free of non-ZSM-48 seed crystals and free of ZSM-50. The low silica ZSM-48 is shown to have improved activity in the dewaxing of slack wax.

[0008] According to the present disclosure, it has now been found that, by using a particular catalyst system comprising a low silica/alumina ratio ZSM-48, it is possible to use a single reactor operating in blocked mode to dewax both low

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and high wax feeds. The catalyst contains a low level of hydrogenation metal and, even using high wax feeds, is sufficiently active to allow the dewaxing to be effected at commercially acceptable throughput rates and at temperatures which minimize the undesirable dry gas (C₄) make. The catalyst is also able to process feeds containing higher levels of nitrogen and sulfur than a lower activity catalyst could handle.

SUMMARY

[0009] In one aspect, the disclosure resides in a catalytic dewaxing process comprising:

(a) providing in a reaction zone a catalyst comprising from 40 to 80 wt% of ZSM-48 having a silica to alumina molar ratio of less than 200:1 and from 0.3 to 1.5 wt% of a metal or metal compound from Groups 8 to 10 of the Periodic Table of the Elements; and

(b) periodically contacting said catalyst in said reaction zone under dewaxing conditions with a first hydrocarbon feedstock having a wax content of less than 50 wt% and with a second hydrocarbon feedstock having a wax content of 50 wt% or more.

[0010] Conveniently, the catalyst comprises from 50 to 70 wt% of ZSM-48 having a silica to alumina molar ratio of less than 200:1. In one embodiment, the ZSM-48 has a silica to alumina molar ratio of 100:1 or less.

[0011] Conveniently, the catalyst comprises from 0.3 to 0.8 wt% of a metal or metal compound from Groups 8 to 10 of the Periodic Table of the Elements, especially platinum.

[0012] Conveniently, the catalyst further comprises an inorganic oxide binder, such as silica, a silicate, or an aluminosilicate.

[0013] Conveniently, said dewaxing conditions include a temperature of 365°C or less, such as from 290°C to 365°C, and a liquid hourly space velocity on the hydrocarbon feed of at least 0.4 hr⁻¹, such as from 0.95 to 3 hr⁻¹.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] **Figure 1** is a graph comparing the average reaction temperature required to achieve different final pour points with high and low sulfur hydrotreated slack wax feeds using the dewaxing process of Example 3.

[0015] **Figure 2** is a graph comparing the 370°C+ conversion required to achieve different final pour points with high and low sulfur feeds hydrotreated slack wax feeds using the dewaxing process of Example 3.

[0016] **Figure 3** is a graph comparing the average reaction temperature required to achieve different final pour points with different feeds using the dewaxing catalyst of Example 1 and using a similar process but with a higher silica to alumina ZSM-48 catalyst.

[0017] **Figure 4** is a graph comparing the 370°C+ conversion required to achieve different final pour points with different feeds using the dewaxing catalyst of Example 1 and using a similar process but with a higher silica to alumina ZSM-48 catalyst.

DETAILED DESCRIPTION

[0018] All numerical values within the detailed description and the claims herein are modified by “about” or “approximately” the indicated value, and take into account experimental error and variations that would be expected by a person having ordinary skill in the art.

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[0019] Described herein is a process for dewaxing hydrocarbon feedstocks that contain widely varying levels of wax, for example from slack waxes containing in excess of 90 wt% wax to a hydrocrackate containing less than 20 wt% wax, using a single catalyst in a single reactor in blocked operation. In the present context, the term “blocked operation” means that, in dewaxing a first hydrocarbon feedstock having a wax content of less than 50 wt% and a second hydrocarbon feedstock having a wax content of 50 wt% or more, the first feedstock would, for example, be contacted with the catalyst under dewaxing conditions for a certain period of time. The supply of the first feedstock to the reactor would then be terminated or blocked, and the second feedstock would be supplied to the reactor without change-out of the catalyst but normally with the dewaxing conditions being changed to deal with the higher wax content of the feed.

[0020] The present process employs a dewaxing catalyst comprising from 40 to 80 wt%, such as from 50 to 70 wt%, of ZSM-48 zeolite having a silica to alumina molar ratio of less than 200:1, typically 100:1 or less, and from 0.3 to 1.5 wt%, such as from 0.3 to 0.8 wt%, of a hydrogenation metal or metal compound from Groups 8 to 10 of the Periodic Table of the Elements. Generally, the metal or metal compound from Groups 8 to 10 is platinum or a compound thereof and is incorporated in the catalyst by impregnation or ion exchange.

[0021] ZSM-48 is a zeolite having 10-ring unidirectional pores. ZSM-48, its X-ray diffraction pattern and a method for its preparation are described in each of U.S. Patent Nos. 4,375,573, 4,397,827, 4,448,675 and 4,423,021. However, as conventionally synthesized, ZSM-48 has a silica/alumina molar ratio in excess of 200:1.

[0022] The low silica/alumina ZSM-48 employed in the present process can be prepared by crystallizing a reaction mixture comprising silica, alumina, base, water and a directing agent (R) comprising a hexamethonium (N,N,N,N',N',N'-hexamethyl-1,6-hexanediammonium) salt, particularly

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hexamethonium dichloride or dihydroxide. Typically, the reaction mixture has the following composition.

SiO ₂ :Al ₂ O ₃	70 to 110
H ₂ O: SiO ₂	1 to 500
OH ⁻ : SiO ₂	0.1 to 0.3, preferably 0.14 to 0.18
R: SiO ₂ =	0.01-0.05, preferably 0.015 to 0.025

[0023] The crystallization is generally conducted by stirring the reaction mixture at a temperature of 100 to 250°C and produces ZSM-48 crystals having a silica:alumina molar ratio of 70 to 110 and a crystal size in the range of 0.01 to 1 μm. More information on this process for producing low silica/alumina ZSM-48 can be found in U.S. Published Patent Application No. 2007/0131581, the entire contents of which are incorporated herein by reference.

[0024] In addition to the ZSM-48 and hydrogenation metal, the catalyst employed in the present process typically also contains from 20 to 60 wt% of a binder or matrix material. Binders are attrition resistant and resistant to the temperatures experienced by the catalyst in use. Binders may be catalytically active or inactive and include other zeolites, other inorganic materials such as clays and metal oxides, such as alumina, titania, silica and silica-alumina. Clays may be kaolin, bentonite and montmorillonite and are commercially available. Other suitable porous matrix materials in addition to silica-aluminas include other binary materials such as silica-magnesia, silica-thoria, silica-zirconia, silica-beryllia and silica-titania as well as ternary materials such as silica-alumina-magnesia, silica-alumina-thoria and silica-alumina-zirconia.

[0025] The present process can be employed in the isomerization dewaxing of a wide variety of lube oil feedstocks. Such feedstocks are generally wax-containing feeds that boil in the lubricating oil range, typically having a 10% distillation point greater than 650°F (343°C), measured by ASTM D 86 or

ASTM D2887. Such feeds may be derived from a number of sources such as oils derived from solvent refining processes such as raffinates, partially solvent dewaxed oils, deasphalted oils, distillates, hydrocracker bottoms, vacuum gas oils, coker gas oils, slack waxes, foots oils and the like, and Fischer-Tropsch waxes. Preferred feeds are slack waxes and Fischer-Tropsch waxes. Slack waxes are typically derived from hydrocarbon feeds by solvent or propane dewaxing. Slack waxes contain some residual oil and are typically deoiled. Foots oils are derived from deoiled slack waxes. Fischer-Tropsch waxes are prepared by the Fischer-Tropsch synthetic process.

[0026] The feedstocks employed in the present process may have high contents of nitrogen and/or sulfur contaminants. For example, feeds having a nitrogen content of up to 80 ppm, even up to 150 ppm, and/or a sulfur content of up to 250 ppm, even up 1000 ppm, can be processed in the present process. Sulfur and nitrogen contents may be measured by standard ASTM methods D2622 and D4629, respectively.

[0027] Suitable conditions for the present dewaxing process include temperatures of up to 426°C., preferably 365°C or less, more preferably 290°C to 365°C, pressures of from 791 to 20786 kPa (100 to 3000 psig), preferably 1480 to 17339 kPa (200 to 2500 psig), liquid hourly space velocities of from 0.1 to 10 hr⁻¹, preferably at least 0.4 hr⁻¹, more preferably from 0.95 to 3 hr⁻¹, and hydrogen treat gas rates from 45 to 1780 m³/m³ (250 to 10000 scf/B), preferably 89 to 890 m³/m³ (500 to 5000 scf/B).

[0028] The feedstocks used in the present process may be hydrotreated prior to dewaxing. Suitable hydrotreating catalysts contain Group 6 metals, Group 8-10 metals, and mixtures thereof. Examples of suitable metals include nickel, tungsten, molybdenum, cobalt and mixtures thereof. These metals are typically present as oxides or sulfides on refractory metal oxide supports. The mixture of metals may also be present as bulk metal catalysts wherein the amount of metal is

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30 wt% or greater, based on catalyst. Suitable metal oxide supports include oxides such as silica, alumina, silica-aluminas or titania, preferably alumina. Preferred aluminas are porous aluminas such as gamma or eta. The amount of metal, either individually or in mixtures, ranges from 0.5 to 35 wt%, based on the catalyst.

[0029] Suitable hydrotreating conditions include temperatures of up to 426°C, such as from 150 to 400°C, for example from 200 to 350°C, a hydrogen partial pressure of from 1480 to 20786 kPa (200 to 3000 psig), such as from 2859 to 13891 kPa (400 to 2000 psig), a space velocity of from 0.1 to 10 hr⁻¹, such as from 0.1 to 5 hr⁻¹, and a hydrogen to feed ratio of from 89 to 1780 m³/m³ (500 to 10000 scf/B), preferably 178 to 890 m³/m³.

[0030] The disclosure will now be more particularly described with reference to the following Examples and the accompanying drawings.

EXAMPLES

Example 1

[0031] The dewaxing catalyst employed in this Example comprised of 65 wt% of ZSM-48 having a silica to alumina molar ratio of 90/1 and 35 wt% alumina in the form of a 1.5mm diameter by 3.25mm length quadrulobe extrudate. This extrudate was steamed for 3 hours at 482°C prior to impregnation with 0.3 wt% platinum (as tetraammine platinum nitrate salt). The catalyst was loaded into a vertical downflow reactor beneath a top bed of a hydrotreating catalyst comprising 15 wt% Pt/Pd on alumina.

[0032] The above catalyst combination was used to consecutively hydrotreat and hydroisomerize four different feeds, a light neutral (LN) and a heavy neutral (HN) slack wax and an LN and an HN hydrocrackate having the properties listed

in Table 1. The process was conducted at a liquid hourly space velocity (LHSV) 1 hr^{-1} , a hydrogen circulation rate of $419 \text{ Nm}^3/\text{m}^3$, a pressure of 107 kg/cm^2 and an average reaction temperature adjusted to produce lube fractions having substantially the same pour point. The results are summarized in Table 1.

Table 1

Feed	LN slack wax	HN slack wax	LN Hydrocrackate	HN Hydrocrackate
Density ASTM-287, gm/cc	0.811	0.820	0.839	0.845
Wax Yield D3235, %	94	87	20	20
Sulfur D2622, ppm	5	5	10	10
Nitrogen, ppm	1	1	1	1
Hydroisomerization Conditions				
Temp., °C	351	346	316	315
370°C+ conversion, %	43	32.5	7.2	6.8
Heavy Lube (400+°C) Properties				
Pour Point D5950, °C	-24	-18	-18	-15
VI	141.7	142.8	131	131.7
Yield, wt%	38.1	54.6	70.5	82.8
Noack D5800, wt% (est.)	15	4.3	15	6.5
Light Lube (300-400°C) Properties				
Pour Point D5950, °C	-34	-33	-28	-28
VI	125.7	117.8	119	111
Yield, wt%	26.3	13.6	6.8	5.8
Total lube yield, wt%	64.4	68.2	77.3	88.6
Dry gas, wt%	3.14	2.29	0.60	0.53

[0033] By comparing the required temperatures for reaction (hydroisomerization) versus wax content in Table 1, it can be seen that the light neutral (LN) slack wax required 0.47°C reactor temperature increase per 1% wax in feed (calculated by dividing the 35°C temperature increase required for dewaxing the LN slack wax as compared with the LN Hydrocrackate by the 74

wt% difference in wax content). This is an improvement over the typical value of 0.65-1.0°C per 1% wax in feed and results in lower operating temperatures being required when processing higher wax containing feeds (See Wenlei Cao, “Production of High-Quality Hydrogenated Base Oil Using Isomerization Dewaxing Technology”, Proceedings from China Refining Technology Conference, November 2005 in Zhuhai, China pp 207-218 ISBN 7-80164-888-9). In this Example low gas makes are also achieved some of which is due to catalyst type and some due to low operating temperatures. Even higher wax contents up to 100% are possible, such as GTL type stocks.

Example 2

[0034] This Example is a hypothetical example using the dewaxing catalyst and process conditions of Example 1 to process a similar set of feeds but having higher levels of sulfur and nitrogen impurities. The operating temperatures required to achieve the same 370°C+ conversion as in Example 1 were calculated and the results are shown in Table 2.

Table 2

Feed	LN slack wax	HN slack wax	LN Hydrocrackate	HN Hydrocrackate
Density ASTM-287, g/cc	0.811	0.820	0.839	0.845
Wax Yield D3235, %	94	87	20	20
Sulfur D2622, ppm	27	122	259	250
Nitrogen, ppm	3.5	5	80	80
Hydroisomerization Conditions				
Temp., °C	365	364	364	363
370°C+ conversion, %	43	32.5	7.2	6.8

[0035] Table 2 shows that, depending on the wax content of the feed, high levels of sulfur and nitrogen that can be tolerated at nominal 365°C dewaxing temperature with the catalyst of Example 1. Note that the conversion levels are

the same in Example 2 as Example 1 thus leading to similar lube yields and properties.

Example 3

[0036] In this Example, the dewaxing catalyst of Example 1 was used to dewax two similar slack wax feeds that had undergone prior hydrotreatment with a conventional NiMo on alumina HDT catalyst under similar conditions as specified in Table 3 but with the temperature adjusted to result in hydrotreated products with different sulfur levels.

Table 3

Feed	A	B
HDT Conditions		
H ₂ , circ., Nm ³ /m ³	168	168
Weight average bed temperature (Wabt)	220/230	230/240
LHSV	1.0	1.0
H ₂ cons., Nm ³ /m ³	20	20
Yields		
C1-C6	Nil	Nil
265°C-	Nil	Nil
265-343°C	0.5	0.6
343-370°C	2.4	2.7
370°C+	97.3	96.9
Product Properties		
Sulfur, ppm	18	48
Nitrogen, ppm	1	1
Specific Gravity	0.8140	0.8144
IBP, ASTM D2887	342	341
5%	379	378
50%	426	427
95%	466	466
Oil in wax D3235, %	8	9

[0037] The resultant hydrotreated products were dewaxed to different pour points between -10 and -36°C using the dewaxing catalyst specified in Example 1 and the results are summarized in Figures 1 and 2. The feed properties for dewaxing are shown in Table 3 as “Product Properties” from the hydrotreating step. Figure 1 shows that, although slightly higher temperatures (around 5°C) were required to reach the desired pour point with the higher sulfur content feed, pour points as low as -36°C could still be achieved at reaction temperatures below 365°C. Figure 2 shows that, in terms of conversion of 370°C+ fraction, the impact of the higher sulfur content of feed B was a decreased lube yield of 6-10%. However, both of these results represent a significant improvement over results reported for conventional dewaxing catalysts, where reaction temperatures in excess of 365°C and yield losses of 7-18% were required to achieve similar pour points. (See Wenlei Cao, “Production of High-Quality Hydrogenated Base Oil Using Isomerization Dewaxing Technology”, Proceedings from China Refining Technology Conference, November 2005 in Zhuhai, China pp 207-218 ISBN 7-80164-888-9).

Example 4

[0038] In this Example, the impact of sulfur was determined directly by spiking a heavy hydrocrackate feed with a polysulfide, such as Sulfrzol to 450 ppm dosage. The unspiked feed had the following analysis:

API	37.8
Sulfur D2622, ppm	20
IBP, D2887	560°C
5%	698°C
50	936°C
90	1050°C

[0039] As in Example 1, a dual catalyst was used comprising a top bed of a hydrotreating catalyst comprising 15 wt% Pt/Pd on alumina and a bottom bed of a

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dewaxing catalyst. The dewaxing catalyst comprised 65 wt% of ZSM-48 having a silica to alumina molar ratio of 90/1 and 35 wt% alumina in the form of a 1.5mm diameter by 3.25mm length quadrulobe extrudate. The extrudate was steamed for 3 hours at 482°C prior to impregnation with 0.6 wt% platinum (as tetraammine platinum nitrate salt).

[0040] The feed was treated at a 421 Nm³/m³ hydrogen circulation rate, an LHSV of 1.33 hr⁻¹, a pressure of 1600 psig (11133 kPa) and at the temperatures shown in Table 4. The results are also shown in Table 4 and demonstrate that the high activity catalyst, by allowing dewaxing to be effected at lower temperatures, permits higher sulfur content feeds to be processed while maintaining reasonable lube yields.

Table 4.

Feed	Rx Temp, °C	Pour Point D5950, °C	370°C+ Yield, wt%
No Sulfur	329	-25	88.5
450 ppm S spiked	329	-3	88.0
450 ppm S spiked	337	-18	86.2

Example 5

[0041] Dewaxing of two similar feeds, Feed A: a medium pressure hydrocrackate (MPHC) and Feed B: a lube hydrocrackate (LHDC), were investigated in this Example. The feeds had the properties shown in Table 5.

Table 5

Feed	A	B
API	28.4	28.4
Nitrogen, ppm	6	3
Sulfur D2622, ppm	29	31
IBP, ASTM D2887	508	705
5%	619	768
50%	787	929
90%	896	1047

[0042] The feeds were dewaxed using two different ZSM-48 catalysts. The first catalyst was the same dewaxing catalyst employed in Example 1. The second catalyst comprised 65 wt% of ZSM-48 having a silica to alumina molar ratio of 200/1 and 35 wt% alumina in the form of a 1.5mm diameter by 3.25mm length quadrulobe extrudate. The extrudate was steamed for 3 hours at 482°C prior to impregnation with 0.6 wt% platinum (as tetraammine platinum nitrate salt). The feed was treated at a 421 Nm³/m³ hydrogen circulation rate, an LHSV of 1.33 hr⁻¹, a pressure of 2000 psig (13789 kPa). The results are shown in Figures 3 and 4 and demonstrate that the low silica/alumina ratio catalyst of Example 1 at a Pt content of only 0.3 wt% exhibits similar activity and selectivity (as measured by 370°C+ conversion) to the higher silica/alumina ratio catalyst with a Pt content of 0.6 wt%. This example teaches that the higher zeolite activity can be compensated for by lowering the metal content.

[0043] Feed B used in Example 5 is similar to the feed used in Example 4. Processing conditions are also similar between the two examples, although there is a 400 psig difference in pressure. If one compares the no sulfur result in Example 4 which used a catalyst comprised of 90/1 Si/Al₂ crystal and 0.6 wt% Pt to the Feed B result processed with 0.3 wt% Pt and 90/1 Si/Al₂ ratio, one can see that increasing the metal content from 0.3 wt% to 0.6 wt% increases the catalyst

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activity. Example 4 required only 329°C to achieve a -25°C pour point, while the catalyst from Example 5 with half the metal required approximately 340°C to achieve a similar pour point.

[0044] Applicants have attempted to disclose all forms and applications of the disclosed subject matter that could be reasonably foreseen. However, there may be unforeseeable, insubstantial modifications that remain as equivalents. While the present disclosure has been described in conjunction with specific, exemplary forms thereof, it is evident that many alterations, modifications, and variations will be apparent to those skilled in the art in light of the foregoing description without departing from the spirit or scope of the present disclosure. Accordingly, the present disclosure is intended to embrace all such alterations, modifications, and variations of the above detailed description.

[0045] All patents, test procedures, and other documents cited herein, including priority documents, are fully incorporated by reference to the extent such disclosure is not inconsistent with this disclosure and for all jurisdictions in which such incorporation is permitted.

[0046] When numerical lower limits and numerical upper limits are listed herein, ranges from any lower limit to any upper limit are contemplated.

WHAT IS CLAIMED IS:

1. A catalytic dewaxing process comprising:
 - (a) providing in a reaction zone a catalyst comprising from 40 to 80 wt% of ZSM-48 having a silica to alumina molar ratio of less than 200:1 and from 0.3 to 1.5 wt% of a metal or metal compound from Groups 8 to 10 of the Periodic Table of the Elements; and
 - (b) periodically contacting said catalyst in said reaction zone under dewaxing conditions with a first hydrocarbon feedstock having a wax content of less than 50 wt% and with a second hydrocarbon feedstock having a wax content of 50 wt% or more.
2. The process of claim 1, wherein the catalyst comprises from 50 to 70 wt% of ZSM-48 having a silica to alumina molar ratio of less than 200:1.
3. The process of claim 1 or claim 2, wherein the ZSM-48 has a silica to alumina molar ratio of 100:1 or less.
4. The process of any preceding claim, wherein the catalyst comprises from 0.3 to 0.8 wt% of a metal or metal compound from Groups 8 to 10 of the Periodic Table of the Elements.
5. The process of any preceding claim, wherein said metal or metal compound from Groups 8 to 10 of the Periodic Table of the Elements comprises platinum.
6. The process of any preceding claim, wherein the catalyst further comprises an inorganic oxide binder.

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7. The process of any preceding claim, wherein said dewaxing conditions include a temperature of 365°C or less.

8. The process of any preceding claim, wherein said dewaxing conditions include a temperature of 290°C to 365°C.

9. The process of any preceding claim, wherein said dewaxing conditions include a liquid hourly space velocity on the hydrocarbon feed of at least 0.4 hr⁻¹.

10. The process of any preceding claim, wherein said dewaxing conditions include a liquid hourly space velocity on the hydrocarbon feed of 0.95 to 2 hr⁻¹.

11. The process of any preceding claim, wherein one or both of said first and second hydrocarbon feedstocks has a nitrogen content of up to 150 ppm.

12. The process of any preceding claim, wherein one or both of said first and second hydrocarbon feedstocks has a sulfur content of up to 1000 ppm.