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Multi-phase countercurrent hydrodewaxing process.

A process technique is provided for catalytic hydrodewaxing of heavy petroleum feedstock or the like in a multi-phase catalytic reaction zone containing at least one fixed porous bed of solid catalyst particles which process comprises introducing the heavy feedstock predominately in liquid phase under superatmospheric process conditions at elevated temperature and distributing the feedstock uniformly over the catalyst bed for downward flow in contact with the catalyst; introducing a pressurized reactant gas rich in hydrogen blow the catalyst bed at a rate to establish countercurrent contact dispersed in downcoming liquid; converting a portion of heavy petroleum hydrocarbons by selective cracking thereof to produce a treated liquid product and olefinic byproducts; controlling olefin concentration in the liquid phase by stripping with reactant gas in a lower portion of the catalyst bed thereby enhancing catalyst activity; disengaging upwardly flowing dispersed gas from feedstock above the catalyst bed; and recovering treated petroleum and offgas.

#### MULTI-PHASE COUNTERCURRENT HYDRODEWAXING PROCESS

This invention relates to a process for dewaxing hydrocarbon oils. In particular, it relates to catalytic hydrodewaxing of petroleum oils to produce low pour point distillate and lubricating oil stocks. This invention provides a catalytic reactor operating technique wherein a liquid phase is treated with a gaseous reactant for contacting multi-phase reactants in a fixed porous catalyst bed under continuous countercurrent conditions.

Dewaxing is often required when paraffinic oils are to be used in products which need to have good fluid properties at low temperatures, e.g. lubricating oils, heating oils, jet fuels. The higher molecular weight straight chain normal and slightly branched paraffins which are present in oils of this kind are waves which are the cause of high pour points in the oils. If adequately low pour points are to be obtained, these waxes must be wholly or partly removed. In the past, various solvent refining techniques were used, e.g. propane dewaxing, methyl ethyl ketone (MEK) dewaxing, but the decrease in demand for petroleum waxes, together with the increased demand for gasoline and distillate fuels, has made it desirable to find economic processes which convert waxy components into other materials of higher value. Catalytic dewaxing processes can achieve this by selectively cracking the longer chain paraffins, to produce lower molecular weight products which may be removed by distillation. Processes of this kind are described, for example, in The Oil and Gas Journal, Jan. 6, 1975, pages 69 to 73 and U.S. Patent No. 3,668,113.

It is also known to produce a high quality lube base stock oil by subjecting a waxy crude oil fraction to solvent refining, followed by catalytic hydrodewaxing (HDW) over ZSM-5, with subsequent hydrotreating (HDT) of the lube base stock, as taught in U.S. Patent No. 4.181,598. U.S. Patent No. 4,597,854 (Penick) discloses a continuous multi-bed technique employing alternating beds of dewaxing and hydrogenation catalysts. The dewaxing catalyst is preferably acid nickel ZSM-5.

In order to obtain the desired selectivity, the catalyst has usually been a zeolite having a pore size which admits the straight chain n-paraffins either alone or with only slightly branched chain paraffins, but which generally excludes more highly branched materials, cycloaliphatics and heavy aromatics. Shape-selective zeolites such as ZSM-5, ZSM-11, ZSM-12, ZSM-23, and ZSM-35 have been proposed for this purpose in dewaxing processes, and their use is described in U.S. Patent Nos. 3,894,938, 4,176,050, 4,181,598, 4,222,855, 4,229,282, 4,247,388, 4,257,872, 4,313,817, 4,436,614 and 4,490,242. A dewaxing process employing synthetic offretite is described in U.S. Patent 4,259,174. A hydrocracking process employing zeolite beta as the acidic component is described in U.S. Patent No. 3,923,641.

Dewaxing processes of this kind function by cracking waxy components to form lower molecular weight materials, including olefins and other unsaturated compounds which contribute to deactivation of the catalyst. Cracking products, especially lower olefins, tend to further degrade to form carbonaceous deposits on the catalyst. Coking deactivates the catalyst requiring the process temperature to be raised in order to achieve the desired degree of conversion. As the aging of the catalyst has resulted in the process temperature increasing to an upper limit, the production process is interrupted to permit periodic oxidative regeneration of the catalyst. Frequent shutdown of the production unit for catalyst regeneration can render the dewaxing process less economic.

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Prior work has established the value of metal-exchanged and/or impregnated zeolites, especially acidic Ni-ZSM-5 zeolite, as a hydrodewaxing catalyst. Pd-exchanged ZSM-5 has a lower aging rate than other Group VIII metals, but this requires extra catalyst processing beyond that of the economic standard zeolite employed in commercial HDW processes. It has also been proposed to admix a hydrogenation catalyst, such as palladium on alumina, with a standard HDW catalyst; however, this poses problems in catalyst loading and regeneration techniques. Density differences between the two catalysts make mixed loading difficult.

Chemical reactions between liquid and gaseous reactants present difficulties in obtaining intimate contact between phases. Such reactions are further complicated when the desired reaction is catalytic, and requires contact of both fluid phases with a solid catalyst. Numerous multi-phase reactor systems have been developed wherein a fixed porous bed of solid catalyst is retained in a reactor. Typically, fixed bed reactors have been arranged with the diverse phases being passed concurrently over the catalyst, for instance as shown in U.S. Patents No. 4,126,539 (Derr et al), 4,235,847 (Scott), 4,283,271 (Garwood et al), and 4,396, 538 (Chen et al). In the petroleum refining industry, multi-phase catalytic reactor systems have been employed for dewaxing and other treatments of liquid feedstocks, especially distillates, lubricants, heavy oil fractions, residuum, etc., Other known techniques for contacting liquid-gas mixtures with solid catalysts include slurry catalyst, ebullated bed and countercurrent systems, such as disclosed in U.S. Patents 2,717,202, 3,186,935, 4,221,653, and 4,269,805. While prior reactor systems are satisfactory for

certain needs, efficient multi-phase contact has been difficult to achieve for many fixed bed applications. It has also been found that concurrent hydrodewaxing of petroleum oils yield lower olefinic byproducts which cause rapid deactivation of acid zeolite catalysts or the like.

The present invention provides a unique reactor operation, including countercurrent operating techniques and methods for improved treatment of waxy liquid feedstocks with a hydrogen-containing gaseous reactant in a reactor containing a porous fixed bed of solid catalyst. The present invention further provides such multi-phase reactor operation under controlled flow conditions to maintain desired reactant and byproduct concentrations, while minimizing flow maldistribution patterns and providing optimum volumetric proportions of upwardly moving gas in contact with a downwardly gravitating liquid phase.

A technique has been devised for hydrodewaxing treatment of liquids in a multi-phase catalytic reaction zone containing a fixed porous bed of solid catalyst. The improvement herein comprises the steps of (a) containing the catalyst solids in an enclosed reactor adapted to receive feedstock liquid at the top inlet and reactant gas at a bottom inlet; (b) contacting the liquid feedstock and reactant gas in vertical countercurrent flow through the porous bed to hydrocrack waxy components of the feedstock, thereby producing a dewaxed oil liquid effluent stream and olefinic gas byproduct comprising a mixture of lower olefins in the C<sub>2</sub>-C<sub>12</sub> carbon range; (c) recovering the dewaxed oil liquid effluent stream from the reactor below a lower portion of the porous bed, the dewaxed oil having a substantially decreased pour point and being essentially free of lower olefins; (d) passing the olefinic gas byproduct upwardly through the reactor along with reactant gas for recovery from the reactor above the porous bed, thereby retaining catalyst activity in the lower bed portion, where catalyst activity is particularly important in achieving dewaxing; and (e) controlling hydrogen concentration in the gas phase to provide a maximum hydrogen concentration at the lower bed portion, while decreasing hydrogen partial pressure in the upwardly flowing gas phase inversely to wax component concentration in the downwardly flowing liquid phase.

In the preferred embodiments the catalyst comprises a shape selective medium pore metallosilicate having Bronsted acid activity. This technique is particularly useful in a process for catalytic selective hydrocracking of heavy petroleum feedstock to remove waxy components, reduce pour point and cloud point. These and other features and advantages of the invention will be seen in the following description and drawing.

In the drawings,

Figure 1 is a simplified process diagram showing a vertical reactor with fixed catalyst bed and major flow streams.

Figure 2 is a graphic plot comparing aging characteristics of hydrodewaxing catalyst as a function of reduction in product pour point.

In the process for catalytic hydrodewaxing of a wax-containing oil by contacting a liquid phase waxy oil feedstock with hydrogen-containing reactant gas phase under hydrodewaxing conditions in a porous fixed bed of hydrodewaxing catalyst solids having acid catalytic activity, improved dewaxing can be achieved by employing shape selective medium pore crystalline solid catalysts, especially metallosilicates having a zeolite structure and significant Bronsted acid activity.

Recent developments in zeolite technology have provided a group of medium pore siliceous materials having similar pore geometry. Most prominent among these intermediate pore size zeolites is ZSM-5, which is usually synthesized with Bronsted acid active sites by incorporating a tetrahedrally coordinated metal, such as Al, Ga, B or Fe, within the zeolytic framework. These medium pore zeolites are favored for acid catalysis; however, the advantages of ZSM-5 structures may be utilized by employing highly siliceous material or cystalline metallosilicate having one or more tetrahedral species having varying degrees of acidity. ZSM-5 crystalline structure is recognized by its X-ray diffraction pattern, which is described in U.S. Patent No. 3,702,866 (Argauer, et al.). Various dewaxing catalysts, such as ZSM-11, ZSM-12, ZSM-23, ZSM-35, zeolite beta and other crystalline solids are known for hydrodewaxing, as disclosed in U.S. Patents 3,894,938. 3,923,641, 4,176,050, 4,181,598, 4,213,847, 4,222,855, 4,229,282, 4,247,388, 4,257,872, 4,263,129, 4,313,817, 4,436,614, 4,490,242, 4,597,584, 4,604,261. A standard HDW catalyst useful for the present process is a nickel-treated acidic ZSM-5 zeolite having an acid cracking activity (alpha value) of about 70 to 200 may be employed. A preferred form is a 0.8-2 mm extrudate containing about 65% alumina binder and having a steamed ZSM-5 active component with alpha value of about 90.

Catalyst size can vary widely within the inventive concept, depending upon process conditions and reactor structure. If a low space velocity or long residence in the catalytic reaction zone is permissible, small catalysts having an average maximum dimension of 1 to 5 mm may be employed. However, it is preferred to use larger sizes, e.g., 0.5-2 cm or more, especially when extrudates, rings, saddles or other contact materials are desired. Relatively small catalyst particles may be loaded randomly to assure uniformity and larger supported catalysts may be stacked in a geometric pattern to achieve optimum bed

utilization.

Countercurrent processes for contacting reactant fluids have several advantages. In a single point gas entry system, as the reactant gas rises upwardly from its point of introduction at the bottom of a vertical reactor below the porous bed, it contacts a lower concentration of reactive liquid components. At the point of entry the reactant gas has its greatest concentration. Depletion of the gaseous reactant upwardly will increase the relative concentration of inerts and/or byproduct vapors. Likewise, the liquid being treated is generally more reactive at the upper end of the reactor system where it contacts the depleted rising gaseous phase. Thus, the reactant concentration gradients for countercurrent two-phase systems are opposing. In a typical multi-phase reactor system, the average gas-liquid volume ratio in the catalyst zone is about 1:4 to 4:1 under process conditions.

In those reactions wherein the volume of gas decreases due to reactant depletion, the volumetric ratio of liquid to gas can increase markedly as the liquid feedstock gravitates downwardly through the reactor. In reactions which consume large amounts of hydrogen it may be desirable to have multiple reaction gas feed grids at various levels in the catalyst bed. In general, the quantity of unreacted gas at any particular level should be adequate to provide a mixed phase bulk density of at least 20% of the bulk density of the liquid phase (at reaction conditions). Vapor production, adiabatic heating or expansion can also affect the volume.

Advantageously, the multi-phase reactor system is operated to achieve uniform distribution. If too little liquid flux is maintained, the catalyst surface in the porous bed may be partially coated with a liquid film; however, this trickle mode will permit excessive channeling of the gas phase instead of the desired dispersion characteristics of a reactant froth. Flow rates for both reactant phases are controlled within constraints. Froth formation and disengagement is a function of the liquid viscosity, surface tension, composition and other factors. Advantageously, liquid is uniformly applied across the reactor cross-section above the froth. By detecting and controlling froth level, the proper operation of the reactor can be assured, as disclosed in U.S. Patent 4,550,012 (Penick).

In order to maintain a desirable uniform flow of reactant streams through the fixed catalyst bed, adequate flow paths for liquid and gaseous phases must be provided. In a continuous process the ratio of reactant gas to liquid feedstock and the space velocity of reactants relative to catalyst must be carefully considered. Achievement of uniform vertical flow through a porous bed of solids can be obtained if the catalyst is properly distributed and shaped. The void volume in a reaction zone is a function of catalyst configuration and loading technique. While a densely packed bed of spherical solids may be employed to place a maximum amount of catalyst in a predetermined reactor volume, the low void fraction may interfere with fluid flow, especially where countercurrent flow of two phases is required. Advantageously, the catalyst bed has a high void volume, typically about 0.3 to 0.5 of the bed. Void fractions up to 0.9 can be achieved using loosely packed polylobal or cylindrical extrudates. Hollow ring-type supported catalysts, such as Raschig rings or the like, permit liquids to flow downwardly through the porous bed by gravity while the gas phase reactant rises through the denser liquid, forming dispersed bubbles which contact the wetted catalyst to enhance mass transfer and catalytic phenomena.

Reactor configuration is an important consideration in the design of a continuously operating system. In its simplest form, a vertical cylindrical pressure vessel is provided with a catalyst retaining means and operatively connected for countercurrent fluid flow. A typical vertical reactor having a catalyst bed length to effective diameter (L:D) ratio of about 1:1 to 20:1 is preferred. A single bed or a stacked series of beds may be retained within the same reactor shell. While a reactor of uniform horizontal cross section is disclosed herein, other non-uniform configurations, such as spherical reactors, tapered vessel, etc., may be employed.

Referring to Figure 1, a countercurrent continuous catalytic reactor system is shown for treating a liquid phase with a gaseous reactant. An enclosed reactor shell 10 contains a fixed porous bed 12 of solid catalyst. Upper liquid inlet means 14 is provided for introducing a stream of liquid substantially above the catalyst bed for downward gravity flow through the bed toward lower liquid outlet means 16 for withdrawing treated liquid from the reactor shell. Gas inlet means 20 is disposed below the catalyst bed for introducing a gaseous reactant stream under pressure for countercurrently contacting downwardly flowing liquid in a mixed phase reaction zone, whereby gaseous reactant is dispersed through the liquid phase in intimate contact with the solid catalyst. After passing through a reactant disengagement zone 22 above the catalyst bed 22 through upper gas outlet means, gas is withdrawn from the reactor shell 24. Fluid handling control means such as control module 32 is provided to control fluid stream flow rates. The fluid handling control may include liquid outlet valve means 34 for withdrawing treated liquid at increased rate with increased froth level. Liquid and gas reactant feed rates may be controlled proportionally or as otherwise predetermined by setting control module 32 to operate liquid feed valve means 36 and/or gas feed valve means 38. Inlet flow control may be employed to vary the reactant proportions.

Preferred feedstock comprises waxy petroleum oil and the catalyst comprises crystalline shape

selective metallosilicate medium pore zeolite having Bronsted acid activity. The crystalline shape selective metallosilicate medium pore zeolite catalyst preferably comprises ZSM-5. The predominantly liquid phase is introduced at about 0.2 to 4 LHSV, based on volume of liquid feed per volume of catalyst; and the pressurized reactant gas is introduced at a rate of about 89 to 2670 v/v feedstock (500 to 15,000 std. cubic feet per barrel of feedstock (SCF B)).

The fixed porous bed reactor may be operated at conventional dewaxing temperature of about 200°C to 430°C, and a pressure of about 680 kPa to 20,600 kPa. During the dewaxing operation lower olefinic byproduct of the conversion reaction is stripped from a lower portion of the porous catalyst bed by upwardly flowing reactant gas, and the treated petroleum effluent stream has a concentration of C1-C12 hydrocarbons less than about 0.2 wt. %, preferrably containing less than 0.15% olefinic byproduct.

The stream of liquid hydrocarbon is uniformly applied across the reactor cross-section above the catalyst solids in the fixed porous bed having an average void fraction of about 0.3 to 0.9 enclosed within the reactor shell. Catalyst particles should be of a size (e.g., 1-5mm) that they will not easily be dislodged by the rising gas bubbles. Catalyst holddown screens across the top and perhaps at intermediate points in the reactor bed may be helpful in minimizing catalyst motion. Multiple catalyst beds with means for redistribution between beds may be useful in some applications. The present technique is particularly adapted to treatment of heavy oils with hydrogen-containing gas at elevated temperature.

In the refining of lubricants derived from petroleum by fractionation of crude, a series of catalytic reactions are employed to severely hydrotreat, convert and remove sulfur and nitrogen contaminants, hydrocracking and isomerizing components of the lubricant charge stock in one or more catalytic reactors. This can be followed by hydrodewaxing and/or hydrogenation (mild hydrotreating) in contact with different catalysts under varying reaction conditions.

The advantages of the present invention include: (1) longer liquid residence time in contact with the catalyst than with a typical concurrent downflow reactor or in an entrained up-flow reactor; (2) countercurrent flow pattern will lessen the need for large volumes of gas and alleviate flow maldistribution characteristic of prior art mixed phase concurrent flow; (3) upward flowing gas bubbles serve to agitate the downward moving froth and thus facilitate intimate contact between the gas, liquid, and solid (catalyst) phases.

Advantageously, the present process can be employed with staged hydrodewaxing operations wherein a primary vertical fixed bed reaction zone for partial dewaxing of hydrocarbon feed is operated in series with a secondary vertical fixed bed reaction zone for complete dewaxing. In one embodiment the countercurrent flow of liquid and gas reactants is utilized in both the primary and secondary reaction zones. In another embodiment, only the secondary reaction zone is operated under countercurrent flow conditions of the present invention, with the primary reaction zone operated under conventional concurrent downflow

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Figure 2 catalyst shows aging rate in graphic form, depicting a "pour point wall" as waxy hydrocarbons are treated in a conventional concurrent flow catalytic hydrodewaxing operation to reduce pour point. Rapid aging of the catalyst occurs as the pour point approaches -7°C (20°F). The lubricant-range hydrocarbon feedstocks are Statfjord heavy neutral raffinate (Stock S) and Arabian light neutral (Stock A). The catalyst in each case is a standard steamed nickel-impregnated acidic ZSM-5 zeolite. Less sterically hindered waxy hydrocarbons are initially dewaxed by contact with the catalyst and reactant hydrogen gas to give a product of about 18°C (62°F) pour point. Partially dewaxed hydrocarbons then undergo further hydrodewaxing, usually in a lower region of the reaction zone or in a separate reactor, to yield a final dewaxed hydrocarbon product of about -7°C (20°F) pour point. The more sterically hindered hydrocarbons react in the second stage to give the lower pour point product in the presence of a deleterious amount of by-product lower 45 molecular weight olefins. Such an amount of olefins are known to reduce catalytic activity by coking of the catalyst.

Table I is a comparison of bottom outlet reaction products of a standard two-phase downflow reactor and the countercurrent flow reactor of the present invention. The feedstock in both cases is an Arabian light neutral stock which is contacted with reactant hydrogen gas in a porous catalyst fixed bed comprising catalyst particles containing nickel-treated acidic ZSM-5 extruded with alumina binder in about 0.8 to 2.5 mm (1/32 to 1/10 inch) size and having an average alpha value of about 70 to 200. The fixed bed has a vertical length of about 10 meters and is operated at a pressure of about 2900 kPa (422 psia) and a temperature of about 287°C (550°F) to 354°C (670°F). The liquid hourly space velocity of the heavy waxy Arabian gas oil is about 1 LHSV The flow rate of reactant hydrogen gas is about 445 v/v (2500 SCF/B). The amount of light olefinic hydrocarbons in the liquid bottom effluent is substantially reduced with the countercurrent flow reactor. Hydrocarbons boiling in the range up to about 200°C (400°F) are reduced from 16.3 wt. % of the liquid bottom effluent in the standard cocurrent design to 0.9 wt. % of the liquid effluent in the countercurrent design of the present invention.

TABLE I Standard Two-Phase 5 Countercurrent Downflow Reactor Flow Reactor (Concurrent) 10 Reactor Bottoms (Outlet)(wt. %) 15 4.1 5.1 20 0.1 4.7 25 C<sub>5</sub>-204°C (400°F) 0.8 11.6 Hydrocarbons 30 204-316°C 0.1 (400-600°F) 0.2 35

Hydrocarbons

316°C +

 $(600^{\circ}F +)$ 

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The present process is not limited to dewaxing operations, but can be utilized in a variety of situations where it is advantageous to remove volatile by-products from the lower region of a reaction zone wherein mixed phase reactants contact a porous solid catalyst. In its broader aspects, the discovery relates to a process for controlling the concentration of volatile by-products in an equilibrium chemical conversion reaction comprising the steps of: dispersing a predominantly liquid phase reactant above a fixed bed reaction zone for downward flow in contact with a porous solid catalyst; introducing a pressurized gas comprising at least one reactant below the fixed bed reaction zone for upward flow in contact with the catalyst and countercurrently with the downwardly flowing liquid phase; converting at least a portion of the liquid phase reactant to liquid products and volatile by-products; entraining volatile by-products in the upwardly flowing gas, thereby removing the by-products from the lower region of the reaction zone; disengaging upwardly flowing gas containing volatile by-products from the upper region of the reaction zone; and recovering predominantly liquid phase from the lower region of the reaction zone.

93.9

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79.4

While the invention has been explained by reference to preferred embodiments, there is no intent to limit the inventive concept, except as set forth in the following claims.

#### Claims

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1. A process for catalytic hydrodewaxing of heavy petroleum feedstock in a multi-phase countercurrent catalytic reaction zone containing at least one fixed porous bed of solid medium pore shape selective acid zeolite catalyst particles; characterized in that:

the heavy feedstock predominately in liquid phase is introduced under superatmospheric process conditions at elevated temperature and distributing the feedstock uniformly over the catalyst bed at a liquid hourly space velocity of about 0.2 to 4, based on volume of liquid feedstock per volume of catalyst for downward flow in contact with the catalyst;

a pressurized reactant gas rich in hydrogen is introduced below the catalyst bed at a rate to establish countercurrent contact dispersed in downcoming liquid;

a portion of heavy petroleum waxy hydrocarbons is converted by selective cracking thereof to produce a treated dewaxed liquid petroleum product and  $C_2$ - $C_{12}$  olefinic byproducts;

C<sub>2</sub>-C<sub>12</sub> olefin concentration in the liquid phase is controlled at a concentration less than about 1 wt% by stripping with reactant gas in a lower portion of the catalyst bed, thereby enhancing catalyst activity;

upwardly flowing reactant gas and olefinic byproducts are disengaged from feedstock above the catalyst bed; and

treated petroleum and offgas are recovered.

- 2. The process of Claim 1 wherein the catalyst comprises crystalline shape selective metallosilicate medium pore zeolite having Bronsted acid activity.
- 3. The process of claim 1 wherein the lower olefin byproduct of the conversion reaction is stripped from a lower portion of the porous catalyst bed by upwardly flowing reactant gas.
  - 4. The process of claim 1 wherein the temperature of the fixed porous bed is 200°C to 430°C.
  - 5. The process of claim 1 wherein the pressure of the fixed porous bed is 680 kPa to 20,600 kPa.
- 6. The process of claim 1 wherein the pressurized reactant gas is introduced at a rate of 89 to 2670 v/v feedstock.
  - 7. The process of claim 1, wherein the treated dewaxed petroleum product has a concentration of  $C_{2}$ - $C_{12}$  olefinic hydrocarbons less than about 0.15 wt %.
  - 8. The process of claim 2 wherein the crystalline shape selective metallosilicate medium pore zeolite catalyst comprises ZSM-5.
  - 9. A process for catalytic hydrodewaxing of a wax-containing oil by contacting a liquid phase waxy oil feedstock with hydrogen-containing reactant gas phase under hydrodewaxing conditions in a porous fixed bed of hydrodewaxing catalyst solids having acid catalytic activity; characterized in that:

the catalyst solids are contained in an enclosed reactor adapted to receive feedstock liquid at top inlet and reactant gas at a bottom inlet;

the liquid feedstock and reactant gas are contacted in vertical countercurrent flow through the porous bed to hydrocrack waxy components of the feedstock, thereby producing a dewaxed oil liquid effluent stream and light olefinic byproduct comprising a mixture of lower olefins predominantly in the C2-C12 carbon range;

the dewaxed oil liquid effluent stream is recovered from the reactor below a lower portion of the porous bed, said dewaxed oil having a substantially decreased pour point and being essentially free of lower plefins:

the olefinic gas byproduct is passed upwardly through the reactor along with reactant gas for recovery from the reactor above the porous bed, thereby retaining catalyst activity in the lower bed portion;

hydrogen concentration in the gas phase is controlled to provide a maximum hydrogen concentration at the lower bed portion, while decreasing hydrogen partial pressure in the upwardly flowing gas phase inversely to wax component concentration in the downwardly flowing liquid phase.

- 10. The process for according to Claim 9 wherein the catalyst comprises a shape selective medium pore metallosilicate having Bronsted acid activity; the hydrodewaxing process is conducted at elevated temperature, a liquid hourly space velocity of about 0.2 to 4 parts by volume of oil feedstock per volume of catalyst solids, the catalyst solids having a bed porosity of about 0.3 to 0.9.
  - 11. The process according to Claim 9 wherein the dewaxed liquid effluent stream has a concentration of C·-C·0 hydrocarbons less than about 0.2 wt%.
  - 12. A process for catalytic hydrodewaxing of a wax-containing oil liquid by concurrent contacting of liquid phase waxy oil feedstock with fixed bed of acidic hydrodewaxing catalyst and hydrogen containing-reactant gas in a catalytic hydrodewaxing zone under hydrodewaxing conditions whereby dewaxed liquid oil and by-product olefins are produced, characterized in that:

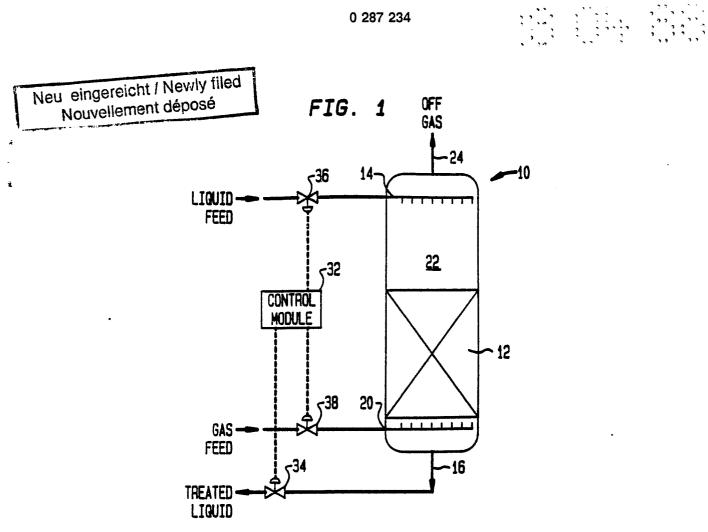
the liquid feedstock is passed downward from top portion of said dewaxing zone in contact with the

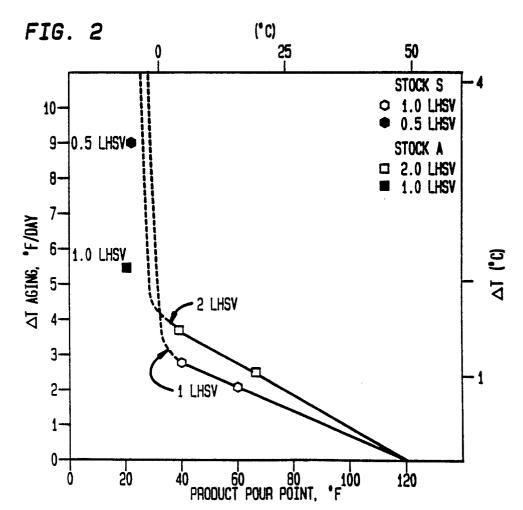
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fixed bed of acidic hydrodewaxing catalyst and in countercurrent contact with the reactant gas under dewaxing conditions at a liquid phase flow rate liquid hourly space velocity of about 0.2 to 0.4 and reactant gas flow rate of 89 to 2670  $v_i v_i$  to strip by-product olefins at a stripping rate sufficient to maintain the bottom portion of the catalyst bed essentially free of  $C_2$ - $C_{12}$  olefins whereby catalyst activity is enhanced: and

dewaxing liquid oil containing less than 0.1 wt % of C<sub>1</sub>-C<sub>4</sub> hydrocarbons is recovered.

- 13. The process of claim 12 wherein the catalyst comprises crystalline shape selective metallosilicate medium pore zeolite having Bronsted acid activity.
- 14. The process of claim 13 wherein the crystalline shape selective metallosilicate medium pore zeolite catalyst comprises ZSM-5.
- 15. The process of claim 12 wherein the dewaxing conditions comprise a temperature of from 200 to 430°C and a pressure of from 680 kPa to 20,600 kPa.
- 16. The process of claim 12 further characterized in that the liquid feedstock, reactant gas and dewaxed liquid oil flow rates are varified by fluid handling control means to control flow maldistribution in the dewaxing zone while maintaining catalytic hydrodewaxing and by-product olefins stripping conditions.





# EUROPEAN SEARCH REPORT

EP 88 30 2775

DOCUMENTS CONSIDERED TO BE RELEVANT					
Category	Citation of document with i	ndication, where appropriate, ssages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)	
Υ	US-A-4 550 012 (J. * Figure 1; claims 1-5 *	E. PENICK) 1-5; column 2, lines	1-16	C 10 G 45/64	
Y	US-A-4 604 261 (N. * Abstract; claims 5, lines 19-39; col column 6, line 19 *	1,2,10,11,12; column umn 5, line 58 -	1-16		
A	US-A-4 211 635 (N. * Figure; claims 1-63 - column 11, lin	10; column 10, line	1-16		
<b>A</b>	US-A-4 213 847 (N. * Figure 1; claims		1-16		
:				TECHNICAL FIELDS SEARCHED (Int. Cl.4)	
				C 10 G	
				·	
	The present search report has t	een drawn up for all claims			
Place of search Date of completion of the search			Examiner		
THE HAGUE		15-07-1988	MICH	MICHIELS P.	
X : part Y : part doc A : tech O : non	CATEGORY OF CITED DOCUME ticularly relevant if taken alone ticularly relevant if combined with an ument of the same category innological background the disclosure transfer disclosure	E : earlier patent after the filing other D : document cite L : document cite	T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons  &: member of the same patent family, corresponding document		

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