

19



Europäisches Patentamt
European Patent Office
Office européen des brevets



11 Publication number:

0 306 164 B1

12

EUROPEAN PATENT SPECIFICATION

- 45 Date of publication of patent specification: **14.10.92** 51 Int. Cl.⁵: **C10M 175/00, C10G 45/02**
- 21 Application number: **88307448.6**
- 22 Date of filing: **11.08.88**

54 **Hydrogenating a temperature sensitive hydrocarbonaceous waste stream.**

30 Priority: **13.08.87 US 84954**

43 Date of publication of application:
08.03.89 Bulletin 89/10

45 Publication of the grant of the patent:
14.10.92 Bulletin 92/42

84 Designated Contracting States:
BE DE ES FR GB IT NL

56 References cited:
EP-A- 0 270 813
EP-A- 0 301 758
FR-A- 2 391 271
US-A- 4 265 733

73 Proprietor: **UOP (a New York general partnership)**
25 East Algonquin Road
Des Plaines Illinois 60017-5017(US)

72 Inventor: **Kalnes, Tom N.**
135 North Dover Street
Lagrange Illinois 60525(US)
Inventor: **James, Robert B.**
1115 Western Avenue
Northbrook Illinois 60062(US)

74 Representative: **Brock, Peter William et al**
UROUHART-DYKES & LORD 91 Wimpole
Street
London W1M 8AH(GB)

EP 0 306 164 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

Description

This invention relates to the production of a hydrogenated distillable and reusable hydrocarbonaceous product stream from a temperature-sensitive hydrocarbonaceous waste stream containing a non-distillable component. More specifically, the invention relates to a process using a combination of flash vaporization and selective hydrogenation for treating a temperature-sensitive hydrocarbonaceous waste stream containing a non-distillable component to produce a hydrogenated distillable and reusable hydrocarbonaceous product stream and a heavy non-distillable product, while minimizing thermal degradation of the hydrocarbonaceous waste stream.

With the advent of recognition of the dangers associated with disposal of waste streams containing hazardous materials, there has been a steadily increasing demand for technology which is capable of treating a temperature-sensitive hydrocarbonaceous waste stream containing a non-distillable component to produce a distillable and reusable hydrocarbonaceous product and a heavy non-distillable product, while minimizing thermal degradation of the hydrocarbonaceous feed stream. Such treatment has always been in demand for the preparation and production of various hydrocarbonaceous products, but with increased emphasis on the treatment and recycle of waste hydrocarbonaceous products for environmental reasons, there is an increased need for improved processes to separate heavy non-distillable components from a distillable hydrocarbonaceous product. For example, during the disposal or recycle of potentially environmentally harmful hydrocarbonaceous waste streams, an important step in the total solution to the problem is the pretreatment or conditioning of a hydrocarbonaceous stream, which facilitates the ultimate resolution to provide product streams which may subsequently be handled in an environmentally acceptable manner. Therefore, those skilled in the art have sought to find feasible techniques to remove heavy non-distillable components from a temperature-sensitive hydrocarbonaceous waste stream to provide a distillable hydrocarbonaceous product. Previously employed techniques include filtration, vacuum wiped film evaporation, solvent extraction, centrifugation, and vacuum distillation.

EP-A-0301758, which is a document to be considered as comprised in the state of the art in accordance with Article 54(3) EPC discloses a process for treating a temperature-sensitive hydrocarbonaceous waste stream containing a non-distillable component to produce a distillable hydrocarbonaceous product and a heavy product comprising the non-distillable component while minimizing thermal degradation of the hydrocarbonaceous stream by

- (a) contacting the hydrocarbonaceous waste stream with a hot first hydrogen-rich gaseous stream having a temperature greater than the hydrocarbonaceous stream in a flash zone to increase the temperature of the hydrocarbonaceous stream and vaporize at least a portion thereof to provide a vapor stream comprising hydrocarbons and hydrogen and a heavy product comprising the non-distillable component;
- (b) condensing at least a portion of the vapor stream to provide a second hydrogen-rich gaseous stream suitable for recycle, and a liquid stream comprising fuel gas and distillable hydrocarbonaceous compounds;
- (c) recovering a distillable hydrocarbonaceous product from the liquid stream and
- (d) heating at least a portion of the second hydrogen-rich gaseous stream, and recycling it to form at least a portion of the first hydrogen-rich gaseous stream.

EP-A-0270813, which is also a document to be considered as comprised in the state of the art in accordance with Article 54(3) EPC discloses a process for the treatment of waste oil which is mixed with hydrogen at an elevated pressure of 50 to 250 bars (5 to 25 MPa), and heated by an external heater to 350 to 500 °C. After separation of solids as a slurry, the vaporized oil rich phase is catalytically hydrogenated at 300 to 400 °C.

The invention provides an improved process for the production of a hydrogenated distillable and reusable hydrocarbonaceous product from a temperature-sensitive hydrocarbonaceous waste stream containing a non-distillable component by contacting the hydrocarbonaceous feed stream with a hot hydrogen-rich gaseous stream to increase the temperature of the feed stream and vaporizing at least a portion of the distillable hydrocarbonaceous compounds, thereby producing a distillable hydrocarbonaceous product which, according to the present invention, is immediately hydrogenated in an integrated hydrogenation zone. Important elements of the improved process are the relatively short time that the feed stream is maintained at elevated temperature, the avoidance of heating the feed stream by indirect heat exchange whereby to preclude the coke formation that could otherwise occur, and the minimization of utility costs due to the integration of the hydrogenation zone.

One embodiment of the invention is a process for treating a temperature-sensitive hydrocarbonaceous waste stream containing a non-distillable component to produce a hydrogenated distillable and reusable hydrocarbonaceous product and a heavy non-distillable product, while minimizing thermal degradation of

the hydrocarbonaceous stream, which comprises (a) contacting the waste stream with a first hydrogen-rich gaseous stream having a temperature greater than the waste stream in a flash zone at flash conditions, thereby increasing the temperature of the waste stream and vaporizing at least a portion thereof to provide a hydrocarbonaceous vapour stream comprising hydrogen, and a heavy product comprising the non-distillable component; immediately (b) catalytically hydrogenating the vapour stream in a hydrogenation reaction zone at hydrogenation conditions to increase the degree of hydrogenation of the hydrocarbonaceous compounds contained in the vapour stream; (c) condensing at least a portion of the resulting effluent from the hydrogenation reaction zone to provide a second hydrogen-rich gaseous stream, suitable for recycle to step (a), and a liquid stream comprising hydrogenated distillable hydrocarbonaceous compounds; and (d) recovering a hydrogenated distillable hydrocarbonaceous product from the liquid stream.

According to another embodiment of the invention the liquid stream obtained in the condensation step (c) is a first liquid stream comprising fuel gas and hydrogenated distillable hydrocarbonaceous compounds, and in step (d) fuel gas is separated from the first liquid stream to provide a second hydrocarbonaceous vapour stream comprising normally gaseous hydrocarbons and a normally liquid hydrogenated distillable hydrocarbonaceous product.

According to yet another embodiment of the invention, the catalytic hydrogenation generates at least one water-soluble inorganic compound by reaction of the hydrocarbonaceous compounds and the effluent from the hydrogenation zone is contacted with a fresh aqueous scrubbing solution, the resulting mixture of effluent and aqueous scrubbing solution is separated to provide the second hydrogen-rich gaseous stream suitable for recycle to step (a), a first liquid stream comprising fuel gas and hydrogenated distillable hydrocarbonaceous compounds, and a spent aqueous scrubbing solution containing at least a portion of the water-soluble inorganic compound; and fuel gas is separated from the first liquid stream to provide a second hydrocarbonaceous vapour stream comprising normally gaseous hydrocarbons and a normally liquid hydrogenated distillable hydrocarbonaceous product.

Other embodiments of the present invention encompass further details such as preferred feedstocks, hydrogenation catalysts, aqueous scrubbing solutions and operating conditions, all of which are hereinafter disclosed in the following discussion of each of these facets of the invention.

The accompanying Drawing is a simplified process flow diagram of a preferred embodiment of the present invention.

The present invention provides an improved integrated process for the removal of heavy non-distillable components from a temperature-sensitive hydrocarbonaceous waste stream and the subsequent hydrogenation of the distillable hydrocarbonaceous stream. A wide variety of temperature-sensitive hydrocarbonaceous waste stream can be treated in accordance with the process of the present invention. Examples of suitable hydrocarbonaceous streams are dielectric fluids, hydraulic fluids, heat transfer fluids, used lubricating oil, used cutting oils, used solvents, still bottoms from solvent recycle operations, coal tars, atmospheric residuum, oils contaminated with polychlorinated biphenyls (PCB), halogenated wastes and other hydrocarbonaceous industrial waste. Many of these hydrocarbonaceous streams may contain non-distillable components which include, for example, organometallic compounds, inorganic metallic compounds, finely divided particulate matter and non-distillable hydrocarbonaceous compounds. The present invention is particularly advantageous when the non-distillable components comprise sub-micron particulate matter, and the conventional techniques of filtration or centrifugation tend to be highly ineffective.

The presence of a non-distillable component including finely divided particulate matter in a hydrocarbonaceous feed to a hydrogenation zone greatly increases the difficulty of the hydrogenation. A non-distillable component tends 1) to foul the hot heat exchange surfaces which are used to heat the feed to hydrogenation conditions, 2) to form coke, or in some other manner deactivate the hydrogenation catalyst, thereby shortening its active life and 3) to hinder in other ways a smooth and facile hydrogenation operation. Particulate matter in a feed stream tends to be deposited within the hydrogenation zone and to plug a fixed hydrogenation catalyst bed, thereby reducing the time on stream.

Once the temperature-sensitive hydrocarbonaceous waste feed stream is separated into a distillable hydrocarbonaceous stream and a heavy non-distillable product, the resulting distillable hydrocarbonaceous stream is introduced into a hydrogenation zone. If the feed stream contains compounds of metals such as zinc, copper, iron, barium, phosphorus, magnesium, aluminium, lead, mercury, cadmium, cobalt, arsenic, vanadium, chromium, and nickel, these compounds will be isolated in the relatively small volume of recovered non-distillable product, which may then be treated for metals recovery, or otherwise disposed of as desired. In the event that the feed stream contains distillable hydrocarbonaceous compounds which include sulphur, oxygen, nitrogen, metal or halogen components, the hydrogenation step will remove or convert such components as desired. In a preferred embodiment of the present invention, the hydrogenation-

tion of the resulting distillable hydrocarbonaceous stream is preferably conducted immediately after flashing the feed, without intermediate separation or condensation. The advantages of the integrated process of the present invention will be readily apparent to those skilled in the art and include the economy of greatly reduced utility costs.

5 The hot first hydrogen-rich gaseous stream preferably comprises more than 70 mole % hydrogen, and more preferably more than 90 mole % hydrogen. The hot hydrogen-rich gaseous stream is multi-functional and serves as 1) a heat source used for direct heating of the hydrocarbonaceous feed stream, to preclude the coke formation that could otherwise occur when using an indirect heating apparatus such as a heater or heat-exchanger, 2) a diluent to reduce the partial pressure of the hydrocarbonaceous compounds during
10 vaporization in the flash zone, 3) a possible reactant to minimize the formation of hydrocarbonaceous polymers at elevated temperatures, 4) a stripping medium and 5) at least a portion of the hydrogen required in the hydrogenation reaction zone. In accordance with the subject invention, the temperature-sensitive hydrocarbonaceous feed stream is preferably maintained at a temperature less than 482 ° F (250 ° C) before being introduced into the flash zone in order to prevent or minimize the thermal degradation of the feed
15 stream. Depending upon the characteristics and composition of the hydrocarbonaceous feed stream, the hot hydrogen-rich gaseous stream is introduced into the flash zone at a temperature greater than the hydrocarbonaceous feed stream, and preferably at a temperature from 200 to 1200 ° F (93 to 649 ° C).

During the contacting, the flash zone is preferably maintained at flash conditions which include a
20 temperature from 150 to 860 ° F (165 to 460 ° C), a pressure from atmospheric to 2000 psig (13788 kPa gauge), a hydrogen circulation rate of 1000 to 30,000 SCFB (168 to 5056 normal m³/m³), based on the temperature-sensitive hydrocarbonaceous feed stream and an average residence time of the hydrogen-containing, hydrocarbonaceous vapour stream in the flash zone from 0.1 to 50 seconds. A more preferred average residence time of the hydrogen-containing, hydrocarbonaceous vapour stream in the flash zone is from 1 to 10 seconds.

25 The resulting heavy non-distillable portion of the feed stream is removed from the bottom of the flash zone as required, to yield a heavy non-distillable product. The heavy non-distillable product may contain a relatively small amount of distillable components, but since essentially all of non-distillable components contained in the hydrocarbonaceous feed stream are recovered in this product stream, the term "heavy non-distillable product" is nevertheless used for the convenient description of this product stream. The
30 heavy non-distillable product preferably contains a distillable component of less than 10 weight percent, and more preferably less than 5 weight percent. Under certain circumstances, with a feed stream not having an appreciable amount of liquid non-distillable components, it is contemplated that an additional liquid may be utilized to flush the heavy non-distillables from the flash zone. An example of this situation is when the hydrocarbonaceous feed stream comprises a very high percentage of distillable hydrocarbonaceous
35 compounds, relatively small quantities of finely divided particulate matter (solid), and essentially no liquid non-distillable component which could act as a carrier for the solids. Such a flush liquid may, for example, be a high boiling range vacuum gas oil having a boiling range from 700 to 1000 ° F (371 to 538 ° C), or a vacuum tower bottoms stream boiling at a temperature greater than 1000 ° F (538 ° C). The selection of a flush liquid depends upon the composition of the hydrocarbonaceous feed stream and the prevailing flash
40 conditions in the flash separator, and the volume of the flush liquid is preferably limited to that required for removal of the heavy non-distillable component.

The resulting hydrogen-containing, hydrocarbonaceous vapour stream is removed from the flash zone and is immediately introduced into a catalytic hydrogenation zone containing hydrogenation catalyst and maintained at hydrogenation conditions. The catalytic hydrogenation zone may contain a fixed, ebullated or
45 fluidized catalyst bed. This reaction zone is preferably maintained under an imposed pressure from atmospheric pressure to 2000 psig (0 to 13790 kPa gauge) and more preferably under a pressure from 100 to 1800 psig (689.5 to 12411 kPa gauge). Suitably, such reaction is conducted with a maximum catalyst bed temperature of 122 to 850 ° F (50 to 454 ° C) selected to perform the desired hydrogenation conversion to reduce or eliminate the undesirable characteristics or components of the hydrocarbonaceous vapour stream.
50 In accordance with the present invention, the desired hydrogenation conversion may be, for example, dehalogenation, desulphurization, denitrification, olefin saturation, oxygenate conversion or hydrocracking. Further preferred operating conditions include liquid hourly space velocities from 0.05 to 20 hr⁻¹ and hydrogen circulation rates from 200 to 50,000 standard cubic feet per barrel (SCFB) (33.71 to 8427 normal m³/m³), preferably from 300 to 20,000 SCFB (50.6 to 3371 normal m³/m³).

55 In the event that the temperature of the hydrogen-containing, hydrocarbonaceous vapour stream which is removed from the flash zone is not deemed to be exactly the temperature selected for the catalytic hydrogenation zone, the temperature of the hydrogen-containing, hydrocarbonaceous stream may be adjusted either upwards or downwards by any means known to those skilled in the art in order to achieve

the desired temperature in the catalytic hydrogenation zone. Such a temperature adjustment may be accomplished, for example, by the addition of either cold or hot hydrogen.

The preferred catalyst composite disposed within the hereinabove described hydrogenation zone can contain a metal component having hydrogenation activity, combined with a suitable refractory inorganic oxide carrier material of either synthetic or natural origin. The precise composition and method of manufacturing the carrier material is not considered essential to the present invention. Preferred carrier materials are alumina, silica and mixtures thereof. Suitable metal components having hydrogenation activity are metals of Groups VI-B and VIII of the Periodic Table, as set forth in the **Periodic Table of the Elements**, E. H. Sargent and Company, 1964. Thus, the catalyst composites may comprise one or more of molybdenum, tungsten, chromium, iron, cobalt, nickel, platinum, palladium, iridium, osmium, rhodium, ruthenium, and mixtures thereof. The concentration of the catalytically active metal component, or components, is primarily dependent upon the particular metal as well as the physical and/or chemical characteristics of the particular hydrocarbon feedstock. For example, metals of Group VI-B are generally present in an amount from 1 to 20 weight percent, the iron-group metals in an amount from 0.2 to 10 weight percent, whereas the noble metals of Group VIII are preferably present in an amount from 0.1 to 5 weight percent, all of which are calculated as if these components existed within the catalyst composite in the elemental state. In addition, any catalyst employed commercially for hydrogenating middle distillate hydrocarbonaceous compounds to remove nitrogen and sulphur may function effectively in the hydrogenation zone of the present invention. It is further contemplated that hydrogenation catalyst composites may comprise one or more of: caesium, francium, lithium, potassium, rubidium, sodium, copper, gold, silver, cadmium, mercury and zinc.

The hydrocarbonaceous effluent stream from the hydrogenation zone is preferably subjected to cooling conditions sufficient to condense at least a portion thereof, and thereafter contacted with an aqueous scrubbing solution. In some instances, the aqueous scrubbing solution may be used to accomplish a portion of the desired condensation. The resulting mixture is admitted to a separation zone in order to separate a spent aqueous stream, a hydrogenated hydrocarbonaceous liquid phase and a hydrogen-rich gaseous phase. The contact of the hydrocarbonaceous effluent from the hydrogenation zone with the aqueous scrubbing solution may be performed in any convenient manner, and is preferably conducted by co-current, in-line mixing, which may be promoted by inherent turbulence, mixing orifices or any other suitable mixing means. The aqueous scrubbing solution is preferably introduced in an amount from 1 to 100 volume percent, based on the hydrocarbonaceous effluent from the hydrogenation zone. The aqueous scrubbing solution is selected depending on the characteristics of the hydrocarbonaceous vapour stream introduced into the hydrogenation zone. For example, if the hydrocarbonaceous vapour stream comprises halogen compounds, the aqueous scrubbing solution preferably contains a basic compound such as calcium hydroxide, potassium hydroxide or sodium hydroxide in order to neutralize the acid such as hydrogen chloride, hydrogen bromide and hydrogen fluoride, for example, which is formed during the hydrogenation of the halogen compounds. In the event that the hydrocarbonaceous vapour stream contains only sulphur and nitrogen compounds, water may be a suitable aqueous scrubbing solution to dissolve the resulting hydrogen sulphide and ammonia. The resulting hydrogenated hydrocarbonaceous liquid phase is recovered and the hydrogen-rich gaseous phase may be recycled to the hydrogenation zone if desired.

The resulting hydrogenated hydrocarbonaceous liquid phase is preferably recovered from the hydrogen-rich gaseous phase in a separation zone which is maintained at essentially the same pressure as the hydrogenation reaction zone and as a consequence contains dissolved hydrogen and low molecular weight normally gaseous hydrocarbons (if present). In accordance with the present invention, it is preferred that the hydrogenation hydrocarbonaceous liquid phase comprising the hereinabove mentioned gases be stabilized in a convenient manner, for example, by stripping or flashing to remove the normally gaseous components to provide a stable hydrogenated distillable hydrocarbonaceous product.

In the Drawing, the process of the present invention is illustrated by means of a simplified flow diagram from which such details as pumps, instrumentation, heat-exchange and heat-recovery circuits, compressors and similar hardware have been omitted as being non-essential to an understanding of the techniques involved. The use of such miscellaneous apparatus is well within the capability of one skilled in the art.

With reference now to the Drawing, a liquid hydrocarbonaceous feed waste stream having a non-distillable component is introduced into the process via conduit (1) and is contacted with a hot gaseous hydrogen-rich recycle stream which is provided via conduit (10) from a source hereinafter described. The liquid hydrocarbonaceous feed waste stream and the hydrogen-rich recycle stream are intimately contacted in hot hydrogen flash separator (2). A hydrocarbonaceous vapour stream comprising hydrogen is removed from separator (2) via conduit (3) and immediately introduced into hydrogenation reaction zone (5) which is maintained at hydrogenation conditions, without intermediate separation thereof. A heavy non-distillable

stream is removed from the bottom of separator (2) via conduit (4) and recovered. The resulting hydrogenated hydrocarbonaceous vapour stream is removed from reaction zone (5) via conduit (6) and is contacted with an aqueous scrubbing solution, which is introduced via conduit (7), to cause condensation of at least a portion of the vapour stream. The resulting mixture of the effluent and the aqueous scrubbing solution is passed via conduit (6) and cooled in heat-exchanger (8) to cause a further portion of the vapour stream to be condensed. The resulting cooled effluent from heat-exchanger (8) is passed via conduit (6) into high pressure vapour/liquid separator (9). A hydrogen-rich gaseous stream is removed from high pressure vapour/liquid separator (9) via conduit (10), heated to a suitable temperature in heat-exchanger (12) and utilized to contact the waste oil feed stream (1) as hereinabove described. Since hydrogen is lost from the process, because a portion of the hydrogen will dissolve in the liquid hydrocarbon product and hydrogen will be consumed during the hydrogenation reaction, it is necessary to supplement the hydrogen-rich gaseous stream with make-up hydrogen from some suitable external source, for example, a catalytic reforming unit or a hydrogen plant. Make-up hydrogen may be introduced into the system at any convenient and suitable point, and is introduced in the embodiment shown in the Drawing via conduit (11). A liquid hydrogenated hydrocarbonaceous stream comprising hydrogen in solution is removed from high pressure vapour/liquid separator (9) via conduit (14) and is introduced into low pressure vapour/liquid separator (15). A spent aqueous scrubbing solution is removed from high pressure vapour/liquid separator (9) via conduit (13) and is recovered. A gaseous stream comprising hydrogen and any normally gaseous hydrocarbons present is removed from low pressure vapour/liquid separator (15) via conduit (17) and recovered. A normally liquid distillable hydrogenated hydrocarbonaceous product is removed from low pressure vapour/liquid separator (15) via conduit (16) and recovered. In the event that the waste oil feed stream contains water, this water is recovered from high pressure vapour/liquid separator (9) via conduit (13) together with the spent aqueous scrubbing solution as hereinabove described.

The process of the present invention is further demonstrated by the following Example.

EXAMPLE

A waste lube oil having the characteristics presented in Table 1 and contaminated with 1020 ppm by weight of polychlorinated biphenyl (PCB) was charged in admixture with a hot hydrogen stream at a rate of 100 mass units per hour to a hot hydrogen flash separation zone. The hot hydrogen was introduced into the hot hydrogen flash separation zone at a rate of 31 mass units per hour.

TABLE 1
WASTE LUBE OIL FEEDSTOCK PROPERTIES

5	Specific Gravity @ 60°F (15°C)	0.8827	
	Vacuum Distillation Boiling Range,	°F	(°C)
	(ASTM D-1160)		
10	IBP	338	(170)
	10%	516	(269)
	20%	628	(331)
15	30%	690	(367)
	40%	730	(388)
	50%	750	(399)
20	60%	800	(421)
	70%	831	(444)
	80%	882	(474)
25	% Over	80	
	% Bottoms	20	
	Sulphur, weight percent		0.5
30	Polychlorinated Biphenyl Concentration, wppm		1020
	Lead, wppm		863
	Zinc, wppm		416
35	Cadmium, wppm		1
	Copper, wppm		21
	Chromium, wppm		5

40 The waste lube oil was preheated to a temperature of <482 °F (<250 °C) before introduction into the hot hydrogen flash separation zone, which temperature precluded any significant detectable thermal degradation. The waste lube oil was intimately contacted in the hot flash separation zone with a hot hydrogen-rich gaseous stream having a temperature upon introduction into the hot hydrogen flash separation zone of >748 °F (>398 °C). In addition, the hot hydrogen flash separation zone was operated at conditions which included a temperature of 748 °F (398 °C), a pressure of 500 psig (3447 kPa gauge), a hydrogen circulation rate of 18,000 SCFB (3034 normal m³/m³) and an average residence time of the vapour stream of 5 seconds. A hydrocarbonaceous vapour stream comprising hydrogen was recovered from the hot hydrogen flash separation zone, and directly and immediately introduced, without separation, into a hydrogenation reaction zone containing a hydrogenation catalyst comprising alumina, cobalt and molybdenum. The hydrogenation reaction is conducted with a catalyst peak temperature of 700 °F (371 °C), a pressure of 500 psig (3447 kPa gauge), a liquid hourly space velocity of 0.5, based on hydrocarbon feed to the hydrogenation reaction zone, and a hydrogen circulation rate of 18,000 SCFB (3034 normal m³/m³). The hydrogenated effluent from the hydrogenation reaction zone, including hydrogen chloride, is contacted with an aqueous scrubbing solution containing sodium hydroxide, cooled to 100 °F (38 °C), and sent to a vapour-liquid high pressure separator wherein a gaseous hydrogen-rich stream is separated from the normally liquid hydrocarbonaceous products and spent aqueous scrubbing solution containing sodium and chloride ions. The resulting gaseous hydrogen-rich stream is heated, and then recycled to the hot hydrogen flash

separation zone, together with a fresh supply of hydrogen in an amount sufficient to maintain the hydrogenation reaction zone pressure. A hydrogenated hydrocarbonaceous stream comprising dissolved hydrogen is removed from the vapour-liquid high pressure separator and introduced into a product stabilizer which is maintained at a pressure of 10 psia (68.9 kPa absolute) and a temperature of 100 °F (38 °C). An overhead gaseous stream in an amount of <1 mass unit per hour and having the characteristics presented in Table 2 is recovered from the hereinabove mentioned product stabilizer.

TABLE 2

ANALYSIS OF PRODUCT STABILIZER OVERHEAD GAS STREAM	
Component	Mole Percent
Hydrogen	53.3
C ₁	15.4
C ₂	9.0
C ₃	7.9
C ₄	6.4
C ₅	3.8
C ₆ +	4.2

A hydrogenated hydrocarbonaceous liquid stream in an amount of 87.1 mass units per hour, having the characteristics presented in Table 3, is removed from the product stabilizer.

TABLE 3

ANALYSIS OF HYDROGENATED HYDROCARBONACEOUS LIQUID STREAM

Specific Gravity @ 60°F (15°C)	0.855	
Vacuum Distillation Boiling Range, (ASTM D-1160)	°F	(°C)
10%	430	(221)
50%	725	(384)
90%	890	(476)
Sulphur, weight percent		<0.1
Polychlorinated Biphenyl Concentration, wppm		<2
Lead, wppm		<0.03
Zinc, wppm		<0.01
Cadmium, wppm		<0.02
Copper, wppm		<0.01
Chromium, wppm		<0.6

A non-distillable liquid stream is recovered from the bottom of the flash separation zone in an amount of 12 mass units per hour and having the characteristics presented in Table 4.

TABLE 4

ANALYSIS OF NON-DISTILLABLE STREAM	
Specific Gravity @ 60 ° F (15 ° C)	>0.9
Polychlorinated Biphenyl Concentration, wppm	110

Claims

1. A process for treating a temperature-sensitive hydrocarbonaceous waste stream (1) containing a non-distillable component to produce a hydrogenated distillable hydrocarbonaceous product (16) and a heavy product (4) comprising said non-distillable component
 - (a) contacting said waste stream (1) with a first hydrogen-rich gaseous stream (10) having a temperature greater than said waste stream (1) in a flash zone (2) at flash conditions thereby increasing the temperature of said waste stream and vaporizing at least a portion thereof to provide a vapour stream (3) comprising hydrogen and hydrocarbonaceous compounds, and a heavy product stream (4) comprising said non-distillable component; characterized by immediately
 - (b) contacting said vapour stream (3) with a hydrogenation catalyst in a hydrogenation reaction zone (5) at hydrogenation conditions to increase the degree of hydrogenation of the hydrocarbonaceous compounds contained therein;
 - (c) condensing at least a portion of the resulting effluent stream (6) from said hydrogenation reaction zone (5) to provide a second hydrogen-rich gaseous stream (10) and a liquid stream (14) comprising fuel gas and hydrogenated distillable hydrocarbonaceous compounds; and
 - (d) recovering from said liquid stream (14) a hydrogenated distillable hydrocarbonaceous product stream (16) and a fuel gas stream (17); and
 - (e) heating at least a portion of said second hydrogen-rich gaseous stream (10) recovered in step (c) and passing the resulting heated stream back to step (a).
2. A process according to claim 1 characterized in that said temperature-sensitive hydrocarbonaceous waste stream (1) comprises a dielectric fluid, hydraulic fluid, heat transfer fluid, used lubricating oil, used cutting oil, used solvent, still bottoms from a solvent recycle operation, coal tar, atmospheric residuum, PCB-contaminated oil, halogenated waste or other hydrocarbonaceous industrial waste, and said non-distillable component comprises an organometallic compound, inorganic metallic compound, finely divided particulate matter or non-distillable hydrocarbonaceous compound.
3. A process according to claim 1 or 2 characterized in that said temperature-sensitive hydrocarbonaceous waste stream (1) is introduced into said flash zone (2) at a temperature less than 482 ° F (250 ° C), and wherein the temperature of said hot first hydrogen-rich stream (10) is from 200 to 1200 ° F (93 to 649 ° C).
4. A process according to any one of claims 1 to 3 characterized in that said flash conditions include a temperature from 150 to 860 ° F (65 to 460 ° C), a pressure from atmospheric to 2000 psig (13788 kPa gauge), a hydrogen circulation rate of 1000 SCFB to 30,000 SCFB (168 to 5056 normal m³/m³), based on said temperature-sensitive hydrocarbonaceous waste stream, and an average residence time of said vapour stream in said flash zone (2) of 0.1 to 50 seconds.
5. A process according to any one of claims 1 to 4 characterized in that said hydrogenation reaction zone (5) is operated at conditions which include a pressure from atmospheric to 2000 psig (0 to 13790 kPa gauge), a maximum catalyst temperature from 122 to 850 ° F (50 to 454 ° C) and a hydrogen circulation rate from 200 to 50,000 SCFB (33.7 to 8427 normal std m³/m³).
6. A process according to any one of claims 1 to 5 characterized in that said hydrogenation catalyst comprises a refractory inorganic oxide and at least one compound having hydrogenation activity of a metal of Group VIB or VIII of the Periodic Table.
7. A process according to any one of claims 1 to 6 wherein at least one water-soluble inorganic compound is produced in hydrogenation reaction zone (5) characterized in that the effluent (6) from

said hydrogenation zone (5) containing hydrogenated hydrocarbonaceous compounds and at least one water-soluble inorganic compound is contacted with a fresh aqueous scrubbing solution (7); and the resulting mixture of effluent (6) and scrubbing solution (7) is passed into a separation zone (9) to provide a second hydrogen-rich gaseous stream (10), a first liquid stream (14) comprising fuel gas and hydrogenated distillable hydrocarbonaceous compounds, and a spent aqueous scrubbing solution (13) containing at least a portion of said water-soluble inorganic compound.

8. A process according to claim 7 characterized in that the water-soluble inorganic compound is hydrogen sulphide, ammonia, hydrogen chloride, hydrogen bromide or hydrogen fluoride, and the scrubbing solution comprises calcium hydroxide, potassium hydroxide or sodium hydroxide.
9. A process according to any one of claims 1 to 8 characterized in that an additional liquid is employed to flush heavy non-distillable components from the flash zone.

Patentansprüche

1. Verfahren zur Behandlung eines temperaturempfindlichen Kohlenwasserstoff-Abfallstromes (1), der eine nichtdestillierbare Komponente enthält, um ein hydriertes destillierbares Kohlenwasserstoffprodukt (16) und ein die nichtdestillierbare Komponente umfassendes schweres Produkt (4) zu erzeugen, indem man

a) den Abfallstrom (1) mit einem ersten wasserstoffreichen Gasstrom (10) mit einer höheren Temperatur als der Abfallstrom (1) in einer Entspannungszone (2) bei Entspannungsbedingungen in Berührung bringt und so die Temperatur des Abfallstromes erhöht und wenigstens einen Teil desselben unter Bildung eines Wasserstoff und Kohlenwasserstoffverbindungen umfassenden Dampfstromes (3) und eines die nichtdestillierbare Komponente umfassenden schweren Produktstromes (4) verdampft,

dadurch gekennzeichnet, daß man unmittelbar

b) den Dampfstrom (3) mit einem Hydrierkatalysator in einer Hydrierzone (5) bei Hydrierbedingungen behandelt, um den Hydrierungsgrad der darin enthaltenen Kohlenwasserstoffverbindungen zu erhöhen,

c) wenigstens einen Teil des resultierenden Auslaufstromes (6) aus dieser Hydrierzone (5) kondensiert, um einen zweiten wasserstoffreichen Gasstrom (10) und einen Treibstoffgas und hydrierte destillierbare Kohlenwasserstoffverbindung umfassenden flüssigen Strom (14) zu bekommen, und

d) aus diesem flüssigen Strom (14) einen hydrierten destillierbaren Kohlenwasserstoffproduktstrom (16) und einen Treibstoffgasstrom (17) gewinnt und

e) wenigstens einen Teil des in Stufe c) gewonnenen zweiten wasserstoffreichen Gasstromes (10) erhitzt und den resultierenden erhitzten Strom zurück zur Stufe a) führt.

2. Verfahren nach Anspruch 1, **dadurch gekennzeichnet**, daß der temperaturempfindliche Kohlenwasserstoff-Abfallstrom (1) ein dielektrisches Fließmittel, hydraulisches Fließmittel, Wärmeüberführungsfließmittel, verbrauchtes Schmiermittel, verbrauchtes Schneidöl, verbrauchtes Lösungsmittel, Destillationsrückstände aus einer Lösungsmittelrückführung, Kohleteer, atmosphärische Rückstände, PCB-verunreinigtes Öl, halogenierten Abfall oder anderen Kohlenwasserstoffindustrieabfall umfaßt und die nichtdestillierbare Komponente eine metallorganische Verbindung, anorganische Metallverbindung, Feinstoffe oder nichtdestillierbare Kohlenwasserstoffverbindung umfaßt.

3. Verfahren nach Anspruch 1 oder 2, **dadurch gekennzeichnet**, daß der temperaturempfindliche Kohlenwasserstoff-Abfallstrom (1) in die Entspannungszone (2) mit einer Temperatur geringer als 482 °F (250 °C) eingeführt wird, wobei die Temperatur des heißen ersten wasserstoffreichen Stromes (10) 200 bis 1200 °F (93 bis 649 °C) beträgt.

4. Verfahren nach einem der Ansprüche 1 bis 3, **dadurch gekennzeichnet**, daß die Entspannungsbedingungen eine Tempertur von 150 bis 850 °F (65 bis 460 °C), einen Druck von Atmosphärendruok bis 2000 psig (13 788 kPa Überdruok) eine Wasserstoffzirkulationsgeschwindigkeit von 1000 SCFB bis 30 000 SCFB (168 bis 5056 normal-m³/m³), bezogen auf den temperaturempfindlichen Kohlenwasserstoff Abfallstrom, und eine mittlere Verweilzeit des Dampfstromes in der Entspannungszone (2) von 0,1 bis 50 sec einschließen.

5. Verfahren nach einem der Ansprüche 1 bis 4, **dadurch gekennzeichnet**, daß die Hydrierzone (5) bei Bedingungen betrieben wird, die einen Druck von Atmosphärendruck bis 2000 psig (0 bis 13 790 kPa Überdruck), eine maximale Katalysatortemperatur von 122 bis 850 °F (50 bis 454 °C) und eine Wasserstoffzirkulationsgeschwindigkeit von 200 bis 50 000 SCFB (33,7 bis 8427 normal-m³/m³) einschließen.
6. Verfahren nach einem der Ansprüche 1 bis 5, **dadurch gekennzeichnet**, daß der Hydrierkatalysator ein hitzebeständiges anorganisches Oxid und wenigstens eine Verbindung eines Metalles der Gruppe VIB oder VIII des Periodensystems mit Hydrieraktivität umfaßt.
7. Verfahren nach einem der Ansprüche 1 bis 6, bei dem wenigstens eine wasserlösliche anorganische Verbindung in der Hydrierzone (5) erzeugt wird, **dadurch gekennzeichnet**, daß der Ausfluß (6) aus der Hydrierzone (5), welcher hydrierte Kohlenwasserstoffverbindungen und wenigstens eine wasserlösliche anorganische Verbindung enthat, mit einer frischen wäßrigen Waschlösung (7) behandelt wird und das resultierende Gemisch von Ausfluß (6) und Waschlösung (7) in eine Trennzone (9) geführt wird, um einen zweiten wasserstoffreichen Gasstrom (10), einen ersten Treibstoffgas und hydrierte destillierbare Kohlenwasserstoffverbindungen umfassenden flüssigen Strom (14) und eine wenigstens einen Teil der wasserlöslichen anorganischen Verbindung enthaltende verbrauchte wäßrige Waschlösung (13) zu bekommen.
8. Verfahren nach Anspruch 7, **dadurch gekennzeichnet**, daß die wasserlösliche anorganische Verbindung Schwefelwasserstoff, Ammoniak, Chlorwasserstoffsäure, Bromwasserstoffsäure oder Fluorwasserstoffsäure ist und die Waschlösung Calciumhydroxid, Kaliumhydroxid oder Natriumhydroxid umfaßt.
9. Verfahren nach einem der Ansprüche 1 bis 8, **dadurch gekennzeichnet**, daß eine zusätzliche Flüssigkeit verwendet wird, um schwere, nicht destillierbare Komponenten aus der Entspannungszone zu spülen.

Revendications

1. Procédé de traitement d'un courant hydrocarboné résiduaire sensible à la température, (1) contenant un composant non distillable, pour obtenir un produit hydrocarboné hydrogéné, distillable (16) et un produit lourd (4) comprenant ledit composant non distillable, selon lequel :
- (a) on met en contact ledit courant résiduaire (1) avec un premier courant gazeux riche en hydrogène (10) ayant une température supérieure à celle du courant résiduaire (1), dans une zone d'évaporation flash (2) avec des conditions d'évaporation flash, de façon à accroître ainsi la température dudit courant résiduaire et d'évaporer au moins une partie de celui-ci pour produire un courant de vapeur (3) comprenant de l'hydrogène et des composés hydrocarbonés, et un courant de produit lourd (4) comprenant ledit composant non distillable ;
- caractérisé en ce qu'on effectue immédiatement les étapes consistant :
- (b) à mettre en contact ledit courant de vapeur (3) avec un catalyseur d'hydrogénation dans une zone réactionnelle d'hydrogénation (5) dans des conditions d'hydrogénation, afin d'accroître le degré d'hydrogénation des composés hydrocarbonés contenus dans celui-ci ;
- (c) à condenser au moins une partie de l'effluent résultant (6) issu de la zone réactionnelle d'hydrogénation (5), pour former un deuxième courant gazeux riche en hydrogène (10) et un courant liquide (14) comprenant un gaz combustible et des composés hydrocarbonés hydrogénés distillables ; et
- (d) à récupérer à partir du courant liquide (14), un courant de produit hydrocarboné hydrogéné distillable (16) et un courant de gaz combustible (17) ; et
- (e) à chauffer au moins une partie de ce deuxième courant gazeux riche en hydrogène (10) récupéré dans l'étape (c) et à recycler le courant chauffé résultant dans l'étape (a).
2. Procédé selon la revendication 1, caractérisé en ce que le courant hydrocarboné résiduaire sensible à la température comprend (1) un fluide diélectrique, un fluide hydraulique, un fluide de transfert de chaleur, une huile lubrifiante usée, une huile de coupe usée, un solvant usé, des résidus de distillation issus d'une opération de recyclage de solvant, du goudron de houille, un résidu de distillation atmosphérique, une huile souillée avec du biphényle polychloré, un résidu halogéné ou un autre résidu industriel hydrocarboné, et en ce que le composant non distillable comprend un composé organométal-

EP 0 306 164 B1

lique, un composé métallique inorganique, des particules finement divisées ou un composé hydrocarboné non distillable.

- 5
3. Procédé selon la revendication 1 ou 2, caractérisé en ce que le courant hydrocarboné résiduaire sensible à la température (1) est introduit dans ladite zone de séparation flash (2) à une température inférieure à 482 °F (250 °C), et en ce que la température du premier courant chaud riche en hydrogène (10) est de 200 à 1 200 °F (93 à 649 °C).
- 10
4. Procédé selon l'une quelconque des revendications 1 à 3, caractérisé en ce que les conditions de séparation flash comprennent une température de 150 à 860 °F (65 à 460 °C), une pression allant de la pression atmosphérique jusqu'à 2 000 psig (pression relative : 13 788 kPa), un débit de circulation d'hydrogène de 1 000 SCFB jusqu'à 30 000 SCFB (de 168 à 5 056 m³ dans les conditions normales/m³) par rapport au courant hydrocarboné résiduaire sensible à la température, et un temps de séjour moyen du courant en phase vapeur dans la zone de séparation flash (2) de 0,1 à 50 secondes.
- 15
5. Procédé selon l'une quelconque des revendications 1 à 4, caractérisé en ce que la zone réactionnelle d'hydrogénation (5) est mise en oeuvre dans des conditions comprenant une pression allant de la pression atmosphérique jusqu'à 2 000 psig (pression relative : de 0 à 13 790 kPa), une température maximum de catalyseur allant de 122 à 850 °F (de 50 à 454 °C), et un débit de circulation d'hydrogène de 200 à 50 000 SCFB (de 33,7 à 8 427 m³ dans les conditions normales/m³).
- 20
6. Procédé selon l'une quelconque des revendications 1 à 5, caractérisé en ce que le catalyseur d'hydrogénation comprend un oxyde inorganique réfractaire, et au moins un composé ayant une activité d'hydrogénation, d'un métal du groupe VI-B ou VIII du tableau périodique.
- 25
7. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel on produit au moins un composé inorganique soluble dans l'eau dans la zone réactionnelle d'hydrogénation (5), caractérisé en ce que l'effluent (6) issu de la zone d'hydrogénation (5) contenant des composés hydrocarbonés hydrogénés et au moins un composé inorganique soluble dans l'eau, est mis en contact avec une solution aqueuse d'épuration fraîche (7) ; et en ce que l'on fait passer le mélange effluent résultant (6) et la solution d'épuration (7), dans une zone de séparation (9), pour obtenir un deuxième courant gazeux riche en hydrogène (10), un premier courant liquide (14) comprenant un gaz combustible et des composés hydrocarbonés hydrogénés distillables, et une solution aqueuse d'épuration usée (13) contenant au moins une partie du composé inorganique soluble dans l'eau.
- 30
- 35
8. Procédé selon la revendication 7, caractérisé en ce que le composé inorganique soluble dans l'eau, est le sulfure d'hydrogène, l'ammoniac, le chlorure d'hydrogène, le bromure d'hydrogène, ou le fluorure d'hydrogène et en ce que la solution d'épuration comprend de l'hydroxyde de calcium, de l'hydroxyde de potassium ou de l'hydroxyde de sodium.
- 40
9. Procédé selon l'une quelconque des revendications 1 à 8, caractérisé en ce que l'on emploie un liquide supplémentaire pour purger les composants non distillables lourds à partir de la zone de séparation flash.
- 45
- 50
- 55

