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Señora Jefe de la
DIVISION DE NUEVAS CREACIONES
Superintendencia de Industria y Comercio
E S D

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Trámite 182 PATENTES D
Dependencia 2020 DIVISION DE NUEVAS CREACIONES
Folios 2
511
195
1 REGISTRO/ 538 PETICION

TRÁMITE 002 EVENTO 001 ACTUACIÓN 538

Referencia Expediente No 00-083 187

Asunto Solicitud de patente para METODO Y APARATO
PARA PROCESAR SUMINISTROS DE HIDROCARBUROS
PESADOS

Solicitante ORMAT INDUSTRIES LTD

Fecha de solicitud 01 de noviembre de 2000

Publicada en la Gaceta No 520 del 27 de septiembre de 2002

1 Yo, Emilio FERRERO, identificado como aparece al pie de mi
firma, actuando como apoderado en el asunto de la referencia
atentamente, solicito se efectúe el examen de patentabilidad de la
solicitud en referencia según lo establecido en el artículo 44 de la
Decisión 486 de la Comisión de la Comunidad Andina Para tal efecto
presento junto con este escrito el recibo No 03-21,913 por valor de
\$335 000 00, que corresponde a la tasa fijada según lo dispuesto en la
resolución No 41687 del 24 de diciembre de 2002

2 Ruego atentamente a la Señora Jefe se sirva ordenar que se
anexe este recibo, para que se efectúe dicho examen y se continúe con
el trámite de la solicitud

Bogotá, 26 MAR 2003
Señora Jefe,


EMILIO FERRERO
T P A No 31 929

COLO 11802 801 002 3
MRE/JFR/ID-000023/WPC11802

NIT 860 041 367 3

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115

SUPERINTENDENCIA Y COMERCIO

Radicacion 0083187 00000004 Folios 2

Fecha (AMD) 2003-03-23 17 38 11

Tramite 002 PATENTES D 1 REGISTRO/ 538 PETICION

Dependencia 2028 DIVISION DE NUEVAS CREACIONES

NIT 900174089-2

RECIBO OFICIAL DE CAJA 03 - 21,913
FECHA MARZO 25 DE 2003

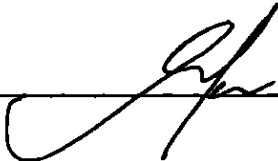
***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No PAGO	FECHA PAGO	Vr PAGO
CAVELIER ABOGADOS	CONSIGNACION	BANCO POPULAR	050-00110-6	9005690	25/03/2003	27,448,920 00

***** CONCEPTO *****

CANT	DETALLE	CONCEPTO	TOTAL CONCEPTO
1	50005-01-01 SOLICITUDES	85 EXAMEN DE PATENTABILIDAD DE INVEN	335,000 00
		TOTAL	\$ 335,000 00

SON TRESCIENTOS TREINTA Y CINCO MIL PESOS

RESPONSABLE 

RECIBO DE CAJA APLICADO AL EXPEDIENTE No _____

066 11802-801-002-3

**SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISION DE NUEVAS CREACIONES**

2020
Bogota, D C , 2 de Agosto de 2005

Doctor
EMILIO FERRERO
Representante **ORMAT INDUSTRIES LTD**

ASUNTO	Radicacion No	00-83187
	Tramite	002
	Evento	001
	Actuacion	430-
	Oficio	3881
	Folios	037

Como resultado del examen de fondo, realizado con fundamento en el articulo 45 de la Decisión 486 de la Comisión de la Comunidad Andina se le comunica

1) Documentos estudiados

- a) Para el presente estudio se tendran en cuenta el capitulo descriptivo comprendido en los folios 2 a 22 de la solicitud en estudio
- b) Para el presente estudio se tendran en cuenta los dibujos comprendidos en los folios 107 a 116 de la solicitud en estudio
- c) Para el presente estudio se tendra en cuenta el capitulo reivindicatorio que comprende 10 reivindicaciones en los folios 23 a 27 de la solicitud en estudio
- d) Conforme lo establece los articulos 9, 10 y 11 de la decisión 486 de la Comisión de la Comunidad Andina, la presente solicitud en estudio fue presentada el 1 de noviembre de 2000, y en el momento de la radicación SI se reclamo prioridad de la primera solicitud presentada en Estados Unidos US 09/431159

2) Objeto de la invencion

- a) Las reivindicaciones 1 a 10 de la solicitud en estudio se refieren a
 - i) Un aparato para procesar un suministro de hidrocarburo pesado que comprende a) un calentador para calentar el suministro de hidrocarburo pesado, b) una torre de fraccionamiento atmosférico para fraccionar el suministro de hidrocarburo pesado calentado hacia la entrada de la torre de fraccionamiento atmosférico lo que produce fracciones atmosféricas livianas y residuos atmosféricos c) otro calentador para calentar los residuos atmosféricos y producir residuos atmosféricos calentados, d) una torre de fraccionamiento atmosférico

para fraccionar los residuos atmosféricos calentados y producir fracciones por vacío livianas y residuos por vacío, e) una unidad de desasfaltado (SDA) para producir crudo desasfaltado (DAO) y asfaltenos a partir del residuo por vacío, f) una unidad de cracking térmico para producir térmicamente el cracking del crudo desasfaltado y producir un producto de cracking térmico que se recicla hacia la entrada de la torre de fraccionamiento atmosférico y g) otra unidad de cracking para producir térmicamente el cracking de las fracciones por vacío livianas para producir otro producto de cracking térmico que se recicla hacia la entrada de la torre de fraccionamiento atmosférico

- ii) Un método para procesar hidrocarburos pesados
- b) El anterior aparato y el anterior procedimiento buscan mejorar el procesamiento de hidrocarburos
- c) Según la Clasificación Internacional de Patentes, la codificación para esta solicitud corresponde a C 10 G 55/00

3) **Determinación del Estado de la Técnica**

El artículo 16 de la Decisión 486 de la Comisión establece

“El estado de la técnica comprenderá todo lo que haya sido accesible al público por una descripción escrita u oral, utilización, comercialización o cualquier otro medio antes de la fecha de presentación de la solicitud de patente o, en su caso, de la prioridad reconocida ”

“Sólo para el efecto de la determinación de la novedad, también se considerará dentro del estado de la técnica, el contenido de una solicitud de patente en trámite ante la oficina nacional competente cuya fecha de presentación o de prioridad fuese anterior a la fecha de presentación o de prioridad de la solicitud de patente que se estuviese examinando, siempre que dicho contenido este incluido en la solicitud de fecha anterior cuando ella se publique o hubiese transcurrido el plazo previsto en el artículo 40 ”

Consultadas las bases de datos y los archivos con que cuenta la entidad, especialmente bajo las clasificaciones **C 10 G 55/00** y las más cercanas a ellas se encontró que antes del 1 de noviembre de 1999 (fecha para determinar el estado de la técnica) habían sido publicados los documentos que se enumeran en la siguiente tabla los cuales se relacionan con aparatos y métodos para procesar hidrocarburos

De acuerdo con lo establecido en el artículo 16 se determinó el estado de la técnica y se encontró el siguiente antecedente

Nº	Documento	Título	Fecha de Publicación
D1	EP 0673 989	Process For the conversion of a residual hydrocarbon oil	1995 09 27
D2	US 4087354	Integrated heat exchange on crude oil and vacuum	1978 05 02
D3	US 4039429	Process for hydrocarbon conversion	1977 08 02

4) Evaluacion de los requisitos de patentabilidad

El articulo 14 de la Decision 486 de la Comision de la Comunidad Andina establece

"Los Paises Miembros otorgaran patentes para las invenciones, sean de producto o procedimiento, en todos los campos de la tecnologia, siempre que sean nuevas tengan nivel inventivo y sean susceptibles de aplicaci3n industrial"

En cumplimiento con este articulo, se procedio a evaluar los requisitos de novedad, nivel inventivo y aplicacion industrial con el fin de establecer la patentabilidad de la invencion reivindicada en la solicitud en estudio

a) Evaluacion del Nivel Inventivo

El art 18 de la Decision 486 de la Comision de la Comunidad Andina establece

"Se considerará que una invencion tiene nivel inventivo, si para una persona del oficio normalmente versada en el arte en la materia tecnica correspondiente, esa invencion no hubiese resultado obvia ni se hubiese derivado de manera evidente del estado de la técnica"

El documento D1 relaciona un proceso para procesar hidrocarburos pesados que contiene practicamente todos los elementos de la actual solicitud Difieren la solicitud actual y D1 en que D1 no incorpora calentadores o calentamiento alguno es sugerido Sin embargo, no es claro como el calentamiento puede marcar una diferencia tan significativa para el proceso Es mas Dichos calentadores ya se han empleado en este tipo de procesos como lo muestra el documento D2 Podria concluirse que el aparato y el metodo reivindicado corresponden a unas formas particulares de lo encontrado en el estado de la tecnica y que por ende no existiria nivel inventivo De la misma forma d3 también sugiere el mismo proceso y el mismo aparato

b) Resumen

En conclusion los requisitos de patentabilidad de la presente solicitud se podrian ver afectados así

Nº	Documento	Reivindicaciones afectadas	Requisito que afecta
D1	EP 0673 989	1 a 10	Nivel inventivo
D2	US 4087354	1 a 10	Nivel inventivo
D3	US 4039429	1 a 10	Nivel inventivo

5) Notificacion

En cumplimiento del articulo 45 de la Decision 486 de la Comision de la Comunidad Andina, se le indica que dentro del termino de sesenta dias contados a partir de la fecha de la notificacion de la presente comunicacion debe responder a la notificación En caso de no dar respuesta al presente requerimiento, o si a pesar de la respuesta subsistieran los impedimentos para la concesion se denegara la patente

Notifiquese el presente oficio conforme a lo dispuesto por el numeral 5 2, literal e) del capitulo quinto del titulo primero de la Circular Unica N° 10 de 2001


ALIX CARMENZA CESPEDES DE VERGEL
Jefe División de Nuevas Creaciones

El anterior requerimiento fue notificado por fijación en la lista, de fecha
13 AGO 2005

Concepto Técnico N°	EXAMINADOR TÉCNICO Codigo No	EXAMINADOR JURÍDICO Código No
1116	202003	



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EUROPEAN PATENT APPLICATION

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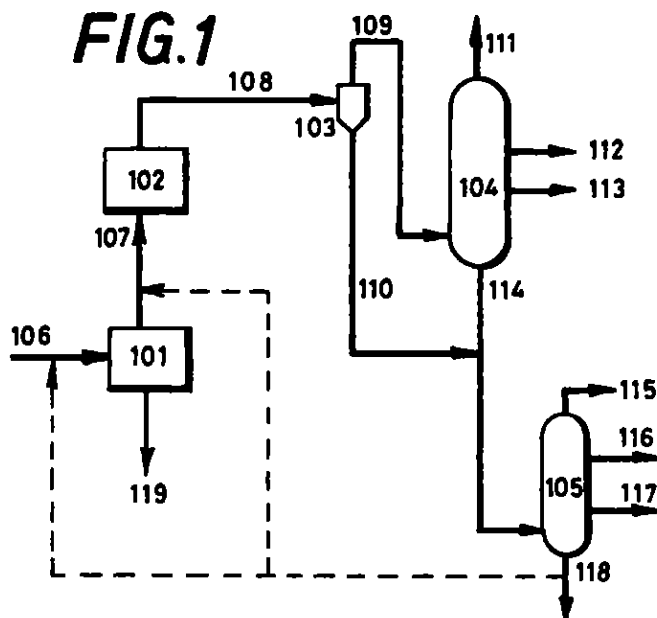
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54 Process for the conversion of a residual hydrocarbon oil

- 57 Process for the conversion of a residual hydrocarbon oil basically comprising the steps of
- (a) deasphalting the residual hydrocarbon oil to obtain a deasphalted oil (DAO) at a yield of at least 50% by weight based on total weight of residual hydrocarbon oil and an asphaltene fraction and
 - (b) passing part or all of the DAO through a thermal cracking zone so that a 520 °C+ conversion of at least 60% by weight based on the total weight of material boiling above 520 °C present in the DAO before thermal cracking is obtained

FIG.1



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The present invention relates to a process for the conversion of a residual hydrocarbon oil

Thermal cracking is a widely and commonly applied route for converting residual hydrocarbon oils into lighter products. It usually involves preheating the feedstock to the appropriate temperature, thermally cracking the preheated feedstock and fractionating the effluent, which often is quenched prior to fractionation in order to stop the cracking reactions. Fractionation may for instance be conducted by atmospheric distillation solely or by a combination of atmospheric and vacuum distillation.

One of the undesired phenomena occurring in thermal cracking of residual oil feedstocks at high conversion levels is the formation of insoluble material limiting the production of distillates. This formation of insoluble material mainly originates from heavy asphaltenic components and to some extent from larger aromatic components present in the feedstocks. Additionally, insoluble material is produced from synthetic asphaltenes formed in condensation reactions occurring in the thermal cracking process. Particularly at severe cracking conditions, formation of insoluble material is known to occur. However, thermal cracking is a relatively simple process requiring a relatively low capital investment and having relatively low operating costs. This makes thermal cracking an attractive option from both a manufacturing and an economic point of view. For this reason, there is a continuous effort for further improving the efficiency of thermal cracking. In the past, several methods have been proposed for achieving this goal.

In NL A 8400074, for instance, a process for producing hydrocarbon mixtures from an oil residue is disclosed, wherein the oil residue is first deasphalted, after which the deasphalted oil is subjected to a cracking process, eventually producing one or more distillate fractions. The asphaltic bitumen fraction is partially oxidised using oxygen to produce a gas mixture containing carbon monoxide and hydrogen, which gas mixture is subsequently used in a catalytic hydrocarbon synthesis to produce synthetic hydrocarbons. These synthetic hydrocarbons are then mixed suitably after having been separated by atmospheric distillation, with at least a part of the said distillate fractions produced in the cracking of the deasphalted oil. The cracking process to which the deasphalted oil is subjected, most suitably, is a catalytic cracking process, because the quality of the light naphtha produced by catalytic cracking is stated to be excellent. A light naphtha produced by thermal cracking, on the other hand, has to be subjected to an additional hydrogenation step for converting dienes into olefins in order to obtain a light naphtha having the desired quality.

In EP A-0 372 652, as a disadvantage of the type of process according to NL A 8400074, is mentioned that the asphaltenes removed from the residual oil in the deasphalting step can no longer contribute to the production of distillates and the yield of distillates is consequently not optimal. Accordingly, the process disclosed in EP A-0 372 652 for converting a heavy hydrocarbonaceous feedstock, such as the vacuum residue of a crude oil, into lighter products involves first preheating the heavy feedstock, after which the preheated feedstock is passed through a thermal cracking zone under such conditions that a conversion of at least 35% by weight, suitably up to 70% by weight, of hydrocarbons having a boiling point of 520 °C or higher is accomplished. The effluent from the cracking zone is subsequently separated into one or more distillate fractions to be recovered as products, and a residual fraction which is deasphalted to obtain an asphalt and a deasphalted oil. This deasphalted oil can be further treated, e.g. by catalytic cracking, hydrotreatment, hydrocracking or thermal cracking, thus yielding more useful distillate fractions. Basically, the process disclosed involves thermal cracking under relatively severe conditions followed by deasphalting of the residual fraction. However, this process is again confronted with the fact that the asphaltenes present in the feedstock for thermal cracking limit the final yield of distillate fractions due to the formation of insoluble and/or coke material, despite the relatively severe cracking conditions. Additionally, the deasphalted oil fraction obtained from the deasphalting treatment of the thermally cracked residual oil fraction still needs further upgrading in additional conversion process units in order to attain conversion into useful distillate products.

Hence, there is still room for improvement of the efficiency of a conversion process involving thermal cracking of residual hydrocarbon oils. It is therefore an object of the present invention to provide a process for converting a residual hydrocarbon oil into lighter products of excellent quality at a high efficiency, both costwise and yieldwise. Regarding the cost-efficiency, it is an object to use as little equipment as possible without affecting the product yield and the quality of the final products. Of course, the process should also meet the appropriate safety and environmental requirements. It is a further object of the present invention to provide a process which can be suitably integrated in various refinery configurations, such as, e.g., a thermal cracker, refinery, a catalytic cracker, refinery, a hydrocracker, refinery, or a refinery which is a combination of two or more of the before mentioned refinery configurations.

Accordingly, the present invention relates to a process for the conversion of a residual hydrocarbon oil comprising the steps of

(a) deasphalting the residual hydrocarbon oil to obtain

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- (i) a deasphalted oil (DAO) at a yield of at least 50% by weight preferably from 80 to 90% by weight more preferably from 85 to 95% by weight based on total weight of residual hydrocarbon oil and
- (ii) an asphaltene fraction and

- (b) passing part or all of the DAO through a thermal cracking zone so that a 520 °C+ conversion of at least 60% by weight preferably from 70 to 90% by weight based on the total weight of material boiling above 520 °C present in the DAO before thermal cracking is obtained

The process of the present invention thus basically involves severe thermal cracking of a deasphalted oil obtained at high yield from a residual hydrocarbon oil

- With the expression 520 °C+ conversion as used throughout this specification is meant the conversion of the hydrocarbons having a boiling point of 520 °C and higher present in the thermal cracking feedstock. The 520 °C+ conversion is conveniently expressed in a weight percentage based on thermal cracking feedstock i.e. DAO and is determined as follows

$$520\text{ }^{\circ}\text{C}+ \text{ conversion} = \frac{520\text{ }^{\circ}\text{C}+ \text{ in feed} - 520\text{ }^{\circ}\text{C}+ \text{ in effluent}}{520\text{ }^{\circ}\text{C}+ \text{ in feed}} \times 100\%$$

- It will be evident that 520 °C+ refers to the amount of hydrocarbons having a boiling point of 520 °C or higher

- An immediate advantage of the process according to the present invention is the fact that the formation of insoluble material during thermal cracking is greatly reduced due to the removal of the heavier asphaltenes from the residual hydrocarbon oil prior to thermal cracking by the deasphalting treatment. As a result the maximum achievable conversion level is now primarily determined by the production of synthetic asphaltene components formed in condensation reactions occurring during thermal cracking instead of by the asphaltene components present in the residual hydrocarbon oil prior to deasphalting. This implies that higher conversion levels with higher distillate productions can be achieved according to the process of the present invention than is the case with severe thermal cracking of residual oils without prior deasphalting this residual oil

- Another advantage of the process according to the present invention is that the quality of the distillate fractions from the thermal cracking zone is very good: the distillate fractions have an excellent H/C ratio and a low content of sulphur and nitrogen containing contaminants. Such contaminants which are present in the residual hydrocarbon oil feedstock were found to mainly concentrate in the asphalt phase produced in the deasphalting treatment rather than in the DAO. Therefore the said contaminants concentrated in the asphalt phase can no longer end up in the distillate fractions produced in the thermal cracking of the DAO.

- Furthermore the process has an excellent synergy potential when included in a thermal cracker refinery, a hydrocracker refinery or a catalytic cracker refinery while incorporation in a refinery which is a combination of two or more of such refinery configurations may offer an even higher synergy potential. For the individual refinery configurations this will be discussed and illustrated in greater detail below by figures 2, 3 and 4.

- The residual hydrocarbon oil used as the feedstock for the process of the present invention in principle may be any residual fraction resulting from a fractionation treatment. Consequently the residual hydrocarbon oil in any event has a relatively high content of asphaltenes. Preferably the residual hydrocarbon oil is a heavy asphaltene-containing hydrocarbonaceous feedstock comprising at least 35% by weight preferably at least 75% by weight and more preferably at least 90% by weight of hydrocarbons having a boiling point of 520 °C or higher. A particularly suitable hydrocarbonaceous feedstock meeting this requirement is a vacuum residue of a crude oil also commonly referred to as a short residue.

- The deasphalting of the residual hydrocarbon oil prior to thermal cracking may be carried out in any conventional manner such as by physical separation using membranes or by adsorption techniques. However for the purpose of the present invention it is preferred to use the well known solvent deasphalting method. In this method the residual hydrocarbon oil to be deasphalted is treated countercurrently with an extracting medium which is usually a light hydrocarbon solvent containing paraffinic compounds. Commonly applied paraffinic compounds include C₃ to C₆ paraffinic hydrocarbons suitably C₃ to C₅ paraffinic hydrocarbons such as propane, butane, isobutane, pentane, isopentane or mixtures of two or more of these. For the purpose of the present invention however it is preferred that butane, pentane or a mixture thereof is used as the extracting solvent whereby the use of pentane is most preferred. In general the extraction depth increases at increasing number of carbon atoms of the extracting solvent. In this connection it is noted that at increasing extraction depth the total amount of heavy hydrocarbons being extracted together with the

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lighter hydrocarbons from the residual hydrocarbon oil increases as well while the asphaltene fraction is smaller but heavier and hence more viscous. Accordingly the extraction depth cannot be too high as this would result in a very viscous very heavy asphaltene fraction which can hardly be processed any further.

In the solvent deasphalting process a rotating disc contactor or a plate column can be used with the residual hydrocarbon oil entering at the top and the extracting solvent entering at the bottom. The lighter hydrocarbons with an overall paraffinic solvency behaviour present in the residual hydrocarbon oil dissolve in the extracting solvent and are withdrawn at the top of the apparatus. The asphaltenic components which are insoluble in the extracting solvent are withdrawn at the bottom of the apparatus. The conditions under which deasphalting takes place are known in the art. Suitably deasphalting is carried out at a total extracting solvent to residual hydrocarbon oil ratio of 1.5 to 8 wt/wt, a pressure of from 1 to 50 bar and a temperature of from 40 to 230 °C. As already described hereinbefore for the purpose of the present invention the deasphalting of the residual hydrocarbon oil is carried out such that a DAO is obtained at an extraction depth of at least 50% by weight, preferably from 60 to 90% by weight, more preferably 65 to 85% by weight, the balance up to 100% by weight being formed by the asphalt fraction. The expression "extraction depth" indicates the yield of DAO after deasphalting by solvent extraction and is expressed in a weight percentage based on total weight of the initial residual hydrocarbon oil prior to deasphalting.

The thermal cracking of the DAO in accordance with the present invention can be carried out by the conventional thermal cracking processes. The exact conditions under which the thermal cracking is carried out can be varied and the person skilled in the art will be able to select the temperature, the pressure and the residence time in such way that the desired conversion occurs. It will be understood that the same conversion can be obtained at a high temperature and a short residence time on the one hand and a lower temperature but longer residence time on the other hand. In order to achieve a 520 °C+ conversion of at least 60% wt on DAO as is required in accordance with the present invention the thermal cracking of the deasphalted oil in the thermal cracking zone is suitably conducted at a temperature of from 350 to 600 °C, a pressure of from 1 to 100 bar and average residence time of from 0.5 to 60 minutes. This residence time relates to the cold feedstock, i.e. the cold oil feedstock at ambient temperature.

The effluent from the thermal cracking zone may be quenched prior to its separation into one or more distillate fractions and a cracked residual fraction. Quenching may for instance be effected by contacting the effluent with a colder quench fluid. Suitable quench fluids include relatively light hydrocarbon oils such as gasoline or a recycled cool residual fraction obtained from the effluent. After the optional quench the effluent is suitably fractionated into one or more distillate fractions and a cracked residual fraction, for instance by atmospheric and/or vacuum distillation. This cracked residual fraction is rather viscous due to the presence of heavy asphaltenic components but is considerably less viscous than the heavy asphalt phase separated from the residual hydrocarbon oil in the deasphalting step.

It is also an aspect of the present invention that the said cracked residual fraction is in part or in total recycled to the residual oil feedstock and/or to the DAO in order to maximise the use of plant capacity and to optimise the distillate production.

In another aspect of the present invention the cracked residual fraction is blended with the more viscous asphalt fraction from the deasphalting treatment and the resulting blendstream is subsequently subjected to partial oxidation (gasification). The blending ratio should be adjusted such that the viscosity of the blendstream meets the viscosity specification of the gasification equipment. The production of a cracked residue which is available as diluent for the more viscous asphalt fraction in the gasifier feedstock offers the possibility to produce an asphalt in the deasphalting treatment with a viscosity exceeding the gasifier feedstock viscosity specification. This implies that a DAO can be produced at higher yield on residual hydrocarbon oil feed and consequently the final production of distillates in the thermal cracking step is higher.

Gasification is suitably carried out using any well known partial oxidation process wherein a heavy hydrocarbonaceous feedstock is partially oxidised using oxygen in the presence of steam, usually high pressure steam, thus resulting in clean gas after gas treatment. This clean gas in return can be applied as clean fuel gas in the refinery or for cogeneration of power and steam, hydrogen manufacture and hydrocarbon synthesis processes.

Figure 1 depicts a typical line up of the process of the present invention.

Figure 2 depicts a line up of a thermal cracking refinery.

Figure 3 depicts a line up of a catalytic cracker refinery.

Figure 4 depicts a line up of a hydrocracker refinery.

According to figure 1 residual hydrocarbon oil (106) preferably a short residue is passed into deasphalting zone (101) resulting in a DAO (107) and an asphalt fraction (119) which is further referred to as "pentane asphalt". The DAO (107) is led into thermal cracking zone (102) where it is heated and where

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the cracking reactions take place. The reaction zone (102) may suitably consist of a furnace alone or of a combination of a furnace plus one or more soaker vessels. Upon leaving the reaction zone (102) the cracked DAO" (108) is passed into cyclone (103) where it is quenched and separated into a cracked residue fraction (110) and a lighter fraction (109). This lighter fraction (109) is separated in atmospheric fractionator (104) into a naphtha minus fraction (111), kerosine fraction (112), gasoil fraction (113) and bottom fraction (114). This bottom fraction (114) is blended with the beforementioned cracked residue fraction (110) and the resulting blend stream is fed into vacuum distillation unit (105) where fractionation takes place into a vacuum gas oil fraction (115), a light flashed distillate (116), a heavy flashed distillate (117) and a vacuum flashed cracked residue (118). The flashed distillates (116) and (117) can be recovered as a product component or can be further upgraded e.g. by further thermal cracking by hydrocracking or by catalytic cracking optionally followed by hydrotreatment. As already mentioned before, the cracked residue (118) may be partially or totally recycled to residual hydrocarbon oil feed (106) and/or to DAO (107) in order to maximise the use of plant capacity and to optimise distillate production. These options are reflected by the dotted lines in figure 1.

In figure 2 crude oil (211) is passed into atmospheric distillation unit (201) and separated into one or more distillate fractions (212) covering all fractions ranging from naphtha minus to heavy gasoil and long residue (213). This long residue (213) is further separated in (high) vacuum distillation unit (202) in vacuum gasoil (214), light flashed distillate (215), heavy flashed distillate (216) and short residue (217). Flashed distillates (215) and (216) are combined and passed into distillate cracking unit (207). Short residue (217) is deasphalted in deasphalting zone (203) resulting in DAO (219) and pentane-asphalt (218). DAO (219) is subsequently subjected to severe thermal cracking (TC) in TC-zone (206) producing, after separation (distillation), distillate fractions (220) which are passed into distillate cracking unit (207) and bottom product (221) which is subsequently passed into vacuum flashing unit (208) together with the bottom product (222) produced in the distillate cracking unit (207). In this vacuum flashing unit (208) separation into thermally cracked flashed distillates (223) and vacuum flashed cracked residue (224) takes place. The thermally cracked flashed distillate fraction (223) is routed to distillate cracking unit (207) and the vacuum flashed cracked residue (224) is added as a diluent to the pentane-asphalt (218) so that the resulting blendstream meets the viscosity specification of gasification unit (204). In the distillate cracking unit (207) there are further produced naphtha minus fraction (225) and gasoil fraction (226) which, after hydrodesulphurization in hydrodesulphurization unit (209), is recovered as valuable automotive gasoil and industrial gasoil components (227). Gasification of the before mentioned blendstream (218/224) takes place by passing this blendstream as well as oxygen (228) and steam (229) into gasification unit (204) where partial oxidation of the heavy hydrocarbons present in the said blendstream takes place to produce a gas mixture (230) mainly consisting of carbon monoxide and hydrogen, which mixture is subsequently purified in gas treatment unit (205). The purified gas (231) can be partially or totally recovered as clean fuel gas in the refinery or can be applied for the cogeneration of power and steam, hydrogen manufacture and/or hydrocarbon synthesis processes.

Compared with a thermal conversion refinery wherein the short residue is thermally cracked without prior deasphalting, the thermal conversion refinery according to figure 2 produces more distillates and less vacuum flashed cracked residue. When deasphalting the short residue at a high extraction depth by using pentane as the extracting solvent, the production of pentane-asphalt is also relatively low. The low production of both vacuum flashed cracked residue and pentane-asphalt means that less gasification capacity is required than with straight severe thermal cracking of short residues, which is attractive from both refinery margin and capital investment point of view.

In the catalytic cracker refinery according to figure 3, a crude oil (310) is separated in atmospheric distillation unit (301) into one or more distillate fractions (311) covering all fractions ranging from naphtha minus to heavy gasoil and long residue (312) which is further separated in (high) vacuum distillation unit (302) into vacuum gasoil (313), light flashed distillate (314), heavy flashed distillate (315) and short residue (316). Short residue (316) is then deasphalted in deasphalting unit (303) resulting in pentane-asphalt (317) and DAO (318) which is passed to TC zone (306) where thermal cracking reactions occur producing, after separation, naphtha minus (319), gasoil fraction (320) and bottom product (321). Bottom product (321) is separated in vacuum flashing unit (307) into thermally cracked flashed distillate fraction (322) and vacuum flashed cracked residue fraction (323). Thermally cracked flashed distillate fraction (322) and light and heavy flashed distillates (314) and (315) are passed into catalytic cracking zone (309) where tops (324), naphtha (325), kerosine (326), light cycle oil (327) and heavy cycle oil/clarified slurry oil (328) are produced. The light cycle oil (327) and gasoil fraction (320) are both passed through hydrodesulphurization unit (308) resulting in valuable automotive and industrial gasoil components (329). Heavy cycle oil/clarified slurry oil (328), pentane asphalt (317) and vacuum flashed cracked residue fraction (323) are blended so that the

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resulting blendstream meets the viscosity specification of gasifier (304) The blendstream oxygen (330) and steam (331) are passed into the gasifier (304) where the heavy hydrocarbons are partially oxidised to produce a gas mixture (332) mainly consisting of carbon monoxide and hydrogen which gas mixture is subsequently purified in gas treatment unit (305) The purified gas (333) can be partially or totally recovered as clean fuel gas in the refinery or can be applied for the cogeneration of power and steam hydrogen manufacture and/or hydrocarbon synthesis processes

Compared with a long residue fluid catalytic cracker (LRFCC) refinery a refinery with a flashed distillate fluid catalytic cracker (FDFCC) and severe thermal cracking of DAO as illustrated by figure 3- has the advantage that no catalyst cooling capacity is required on the FDFCC which means a significant cost saving Additionally contrary to an LRFCC refinery metals present in the crude oil no longer end up on the FCC catalyst in the FDFCC refinery thus reducing costs for FCC catalyst replacement and spent catalyst disposal or rejuvenation Another advantage is the fact that SO_x emissions are strongly reduced in the FDFCC refinery since the major part of the sulphur present in the long residue ends up in the pentane asphalt after deasphalting Sulphur removal in this case takes place in the gasifier gas treating step after partial oxidation of the gasifier feedstock mixture

In the line up of the complex hydrocracker refinery according to figure 4 all reference numbers (401) to (433) have the same meaning as the corresponding reference numbers (201) to (233) in figure 2 The line up according to figure 4 only differs from that according to figure 2 in that flashed distillates (415) and (416) are passed into hydrocracking zone (434) instead of being passed into distillate cracking unit (407) as is the case in figure 2 where flashed distillates (215) and (216) are passed into distillate cracking unit (207) In this hydrocracking zone (434) the flashed distillates (415) and (416) are upgraded i.e. cracked and hydrotreated into tops (435) naphtha (436) kerosene (437) gasoil (438) and hydrowax (439) This hydrowax (439) can suitably be used as a feedstock for a chemical complex e.g. for producing lower olefins It is also noted that the thermally cracked flashed distillate (423) may also be partially or totally used as a feed for the hydrocracking zone (434) instead of being passed into distillate cracking zone (407)

Compared with a refinery with a hydrocracker unit (HCU) on a feedstock consisting of a mixture of flashed distillates and DAO (FD/DAO HCU) the flashed distillate hydrocracker refinery with severe thermal cracking of DAO (FD/HCU + DAO/TC refinery) according to figure 4 has the advantage that a smaller hydraulic capacity of the expensive high pressure HCU is required and that due to the absence of the DAO feed it can be operated at a lower combined feedrate which in return results in a lower reactor volume and hence lower capital investment and operating costs Moreover no expensive high pressure guard bed reactor is required to protect the hydrocracker from metal contaminants and high Conradson Carbon Residue material present in the DAO feedstock Another important advantage of the FD/HCU + DAO/TC refinery according to figure 4 is that due to the upgrading of the DAO via severe thermal cracking the optimum DAO yield on short residue is mainly determined by the blending of the pentane-asphalt with the vacuum flashed cracked residue to meet the maximum viscosity specification of the gasifier feedstock This optimum DAO yield is higher than the optimum DAO yield on short residue in the case of the FD/DAO HCU the latter being predominantly determined by the maximum guard bed reactor Conradson Carbon Residue specification Therefore with the HCU refinery including the severe thermal cracking of DAO more DAO is available for upgrading into valuable distillates resulting in a lower asphalt production a lower capacity requirement for the gasifier unit and hence lower capital investment and operating costs

The invention is further illustrated by the following examples

Example 1

Arabian Heavy Short Residue (AHSR) was deasphalted using pentane as the extracting solvent yielding 70% by weight on AHSR of DAO (AHSR C5-DAO) The extraction was carried out at a total solvent/feed ratio of 2.0 (wt/wt) and a feedstock predilution of 0.5 (wt/wt) at 193 °C and 40 bar pressure The AHSR C5-DAO was subsequently subjected to severe thermal cracking at a pressure of 5.0 bar and at outlet temperatures of 470 480 490 and 500 °C

Comparative Example 1

The same AHSR as used in Example 1 was subjected to thermal cracking at a pressure of 5.0 bar Outlet temperatures were 480 485 470 475 and 481 °C

The analytical data regarding AHSR C5-DAO and AHSR are listed in Table I The following abbreviations are used %w means percent by weight and CST means centistokes

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The results of the thermal cracking of AHSR C5 DAO and AHSR at the different outlet temperatures are listed in Tables II and III respectively

TABLE I

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Data regarding AHSR C5-DAO and AHSR			
		AHSR C5-DAO	AHSR
TBP/GLC			
165 350 C (%w)		1 2	0
350 520 C (%w)		13 3	7 0
520 C + (%w)		85 5	93 0
Density 15/4		0 98	1 03
Viscosity	at 100 C (CSt)	143	2351
	at 150 C (CSt)	24	154
Sulphur (%w)		4 1	5 3
Carbon (%w)		84 4	84 0
Hydrogen (%w)		11 0	10 2
C5 asphaltenes (%w)		1 9	18 9
C7 asphaltenes (%w)		0 1	12 3
Conradson Carbon (%w)		10 2	21 7

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TABLE II

Thermal cracking of AHSR C5-DAO						
5	Expenment No		1	2	3	4
	Outlet temp (C)		470	480	490	500
	Product distribution					
10	C4-(%w)		2 0	3 0	3 9	5 4
	C5 165 C (%w)		4 8	7 7	10 3	16 3
	165 350 C (%w)		10 0	16 5	21 2	26 6
15	350 520 C (%w)		27 7	30 1	31 8	28 3
	520 C + (%w)		55 6	42 7	32 8	23 3
	520 C + conversion on AHSR C5-DAO (%w)		35 0	50 0	61 6	72 7
20	520 C + conversion on AHSR feed (%w)		24 5	35 0	43 1	50 9
	Properties of 350 C + residual fraction					
	Density 15/4		1 01	1 01	1 03	1 04
25	Viscosity	at 100 C (CSt)	79	62	51	57
		at 150 C (CSt)	16	14	12	13
	Sulphur (%w)		4 7	4 8	4 8	5 1
30	Carbon (%w)		84 4	84 6	84 7	84 9
	Hydrogen (%w)		10 3	10 0	9 7	9 2
	C5 asphaltenes (%w)		4 8	9 2	13 9	20 3
35	C7 asphaltenes (%w)		2 7	4 3	8 1	15 7
	Conradson Carbon (%w)		11 4	13 1	15 3	18 4
	Insolubles (%w)		0 01	0 01	0 01	0 03
	520 C + content (%w)		65 5	56 0	47 0	41 4

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TABLE III

Thermal cracking of AHSR							
5	Experiment No		1	2	3	4	5
	Outlet temp (C)		480	485	470	475	481
	Product distribution						
10	C4 (%w)		2 1	2 6	3 1	2 9	3 7
	C5 165 C (%w)		3 7	5 1	6 1	6 7	7 5
	165 350 C (%w)		9 0	12 7	15 7	16 5	18 4
15	350 520 C (%w)		21 5	22 2	22 7	22 4	22 8
	520 C+ (%w)		63 8	57 4	52 4	51 7	49 8
	520 C+ conversion on AHSR feed (%w)		31 5	38 2	43 7	44 4	46 5
	Properties of 350 C+ residual fraction						
	Density 15/4						
20	Viscosity	at 100 C (CSt)	1390	1376	1754	1322	1754
		at 150 C (CSt)	109	108	127	108	127
	Sulphur (%w)		5 50	5 60		5 80	
25	Carbon (%w)		84 3	83 3	84 6	84 5	84 6
	Hydrogen (%w)		9 7	9 4	9 2	9 1	9 0
	C5 asphaltenes (%w)		26 0	27 8	29 3	31 8	31 5
30	C7 asphaltenes (%w)		21 3	22 9	25 0	25 3	25 1
	Conradson Carbon (%w)		20 4	28 2	28 4	28 5	29 6
	Insolubles (%w)		0 13	0 52	0 39	0 54	0 48
35	520 C+ content (%w)		73 9	70 2	67 5	67 7	66 3

At an Insolubles content exceeding about 0.5 %w the thermal cracking pilot plant was found to block due to deposition of insoluble material. As a result further cracking at higher conversion levels was not feasible. Using the DAO-TC route according to example 1 on the other hand resulted in a 350 C+ residual fraction having an insolubles content of only 0.03 %w at an outlet temperature as high as 500 C thus still having potential for further cracking at higher conversion levels without blocking of the pilot plant due to the deposition of insoluble material. In addition hereto it is also evident from comparing the 520 C+ conversion levels relative to the AHSR feed given in tables II and III that the process according to the present invention as illustrated by example 1 allows a higher conversion and hence a higher distillate yield without blocking of the thermal cracking unit by insolubles formed.

Claims

- 1 Process for the conversion of a residual hydrocarbon oil comprising the steps of
- (a) deasphalting the residual hydrocarbon oil to obtain
 - (i) a deasphalted oil (DAO) at a yield of at least 50% by weight preferably from 60 to 90% by weight more preferably from 65 to 85% by weight, based on total weight of residual hydrocarbon oil and
 - (ii) an asphaltene fraction and
 - (b) passing part or all of the DAO through a thermal cracking zone so that a 520 C+ conversion of at least 60% by weight preferably from 70 to 90% by weight based on the total weight of material boiling above 520 C present in the DAO before thermal cracking is obtained

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- 2 A process according to claim 1 wherein the residual hydrocarbon oil is a heavy asphaltene containing hydrocarbonaceous feedstock comprising at least 75% by weight of hydrocarbons having a boiling point of 520 °C or higher
- 5 3. A process according to claim 2 wherein the heavy asphaltene containing hydrocarbonaceous feedstock is a vacuum residue of a crude oil
- 4 A process according to any one of the preceding claims wherein the deasphalting is carried out by solvent extraction using butane pentane or a mixture thereof as the extracting solvent
- 10 5 A process according to claim 4 wherein pentane is used as the extracting solvent.
6. A process according to any one of the preceding claims wherein the deasphalting is carried out at a total extracting solvent to residual hydrocarbon oil ratio of 1.5 to 8 wt/wt a pressure of from 1 to 50 bar and a temperature of from 180 to 230 °C
- 15 7 A process according to any one of the preceding claims wherein thermal cracking of the DAO in the thermal cracking zone is conducted at a temperature of from 350 to 600 °C a pressure of from 1 to 100 bar and average residence time of from 0.5 to 80 minutes
- 20 8. A process according to any one of the preceding claims wherein the cracked residue finally obtained from the thermal cracking zone is partially or totally recycled to the residual hydrocarbon oil feed for the deasphalting treatment and/or to the DAO
- 25 9 A process according to any one of the preceding claims wherein at least a part of the cracked residue finally obtained from the thermal cracking zone and the asphaltene fraction from the deasphalting treatment are blended and the resulting blendstream is subsequently subjected to gasification
- 30 10 A thermal conversion refinery wherein the process according to any one of claims 1 to 9 has been integrated
- 11 A catalytic cracker refinery wherein the process according to any one of claims 1 to 9 has been integrated
- 35 12. A hydrocracker refinery wherein the process according to any one of claims 1 to 9 has been integrated
13. A refinery comprising a combination two or more of the refinery configurations as claimed in claims 10 to 12

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FIG. 1

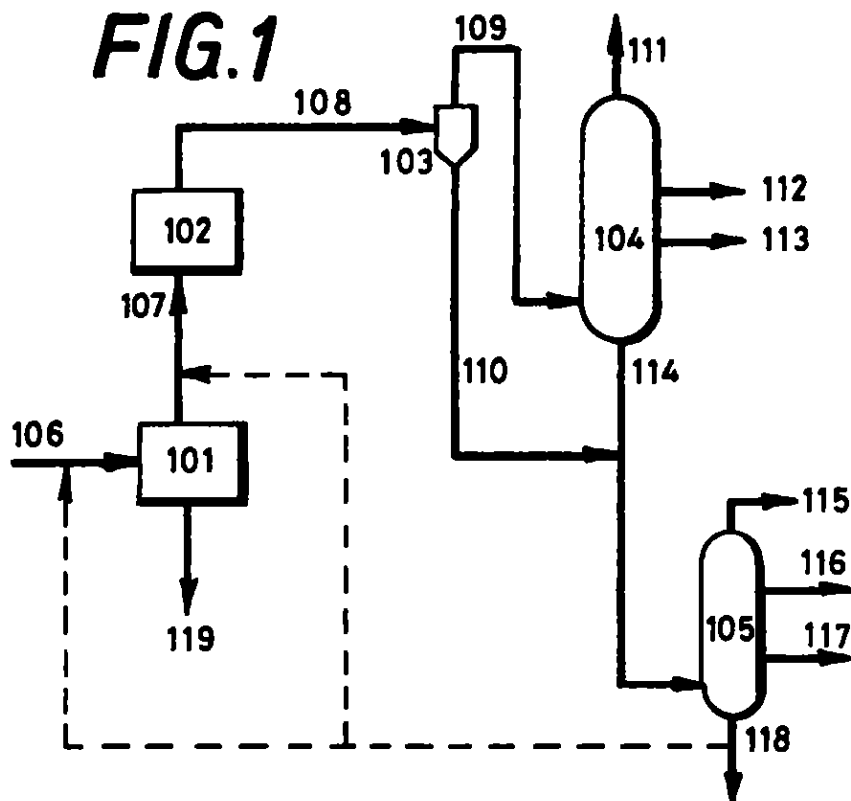
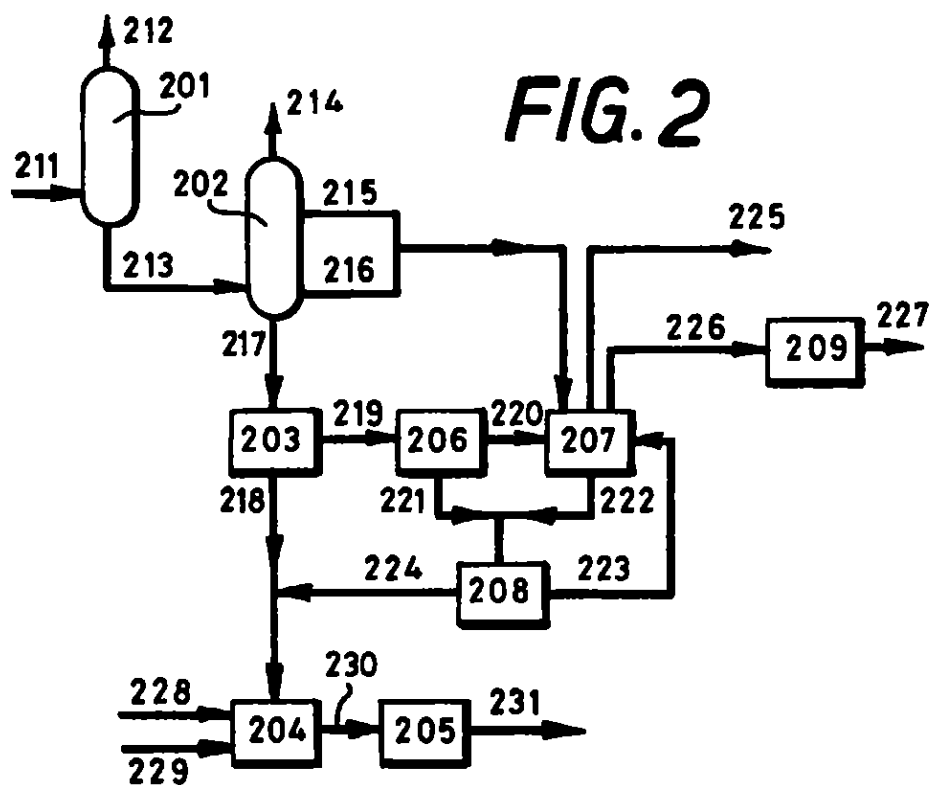
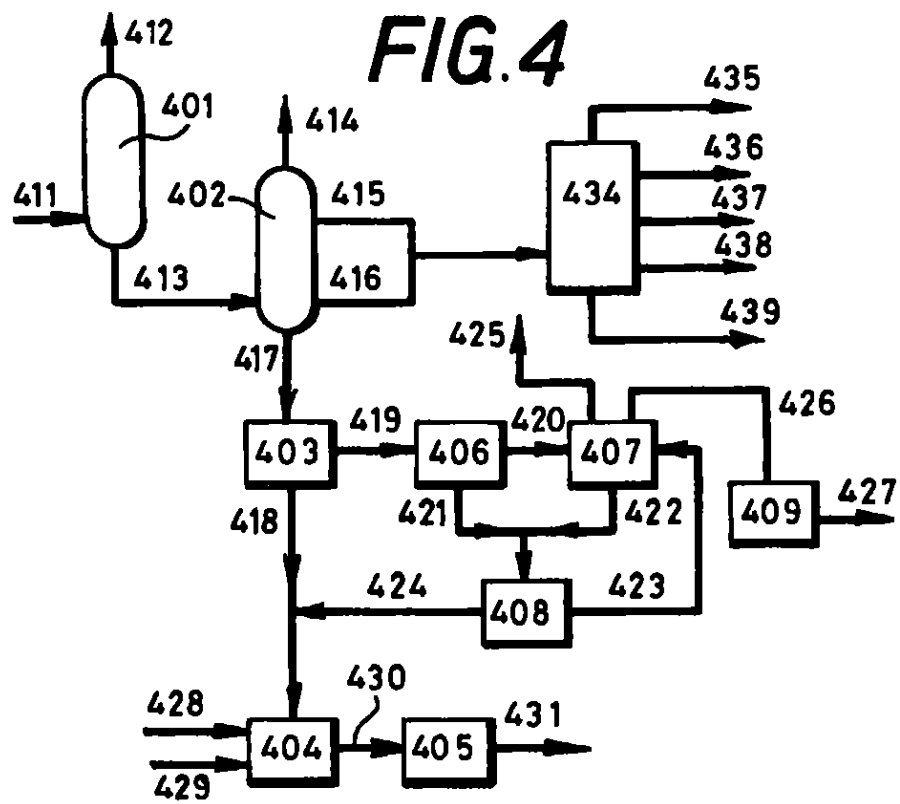
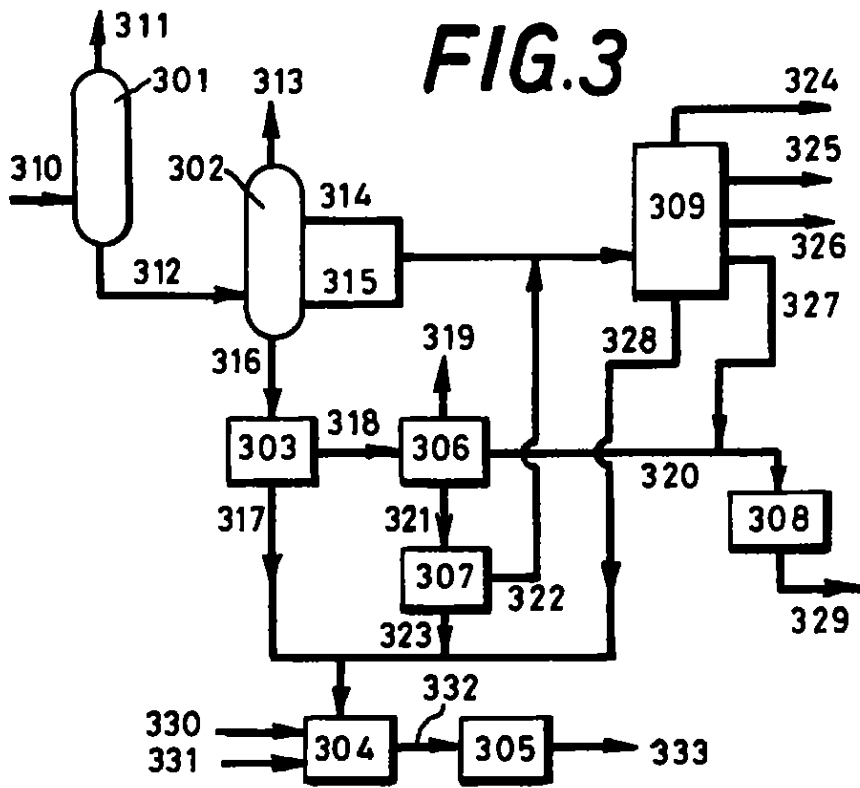


FIG. 2



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[54] INTEGRATED HEAT EXCHANGE ON
CRUDE OIL AND VACUUM COLUMNS

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[51] Int. Cl.² C10G 7/00

[52] U.S. Cl. 208/251 R, 208/353

208/354 208/358

[58] Field of Search 208/251 R 352, 353

208/354 358 365 361

[56] References Cited

U S PATENT DOCUMENTS

1 997 675	4/1935	Bahlke et al	208/365
2,338 595	1/1944	Packue	208/353
2,426,110	8/1947	McCorquodale et al	208/353
3,886,062	5/1975	Peiser et al	208/354
3,888,760	6/1975	Ebert	208/48 R

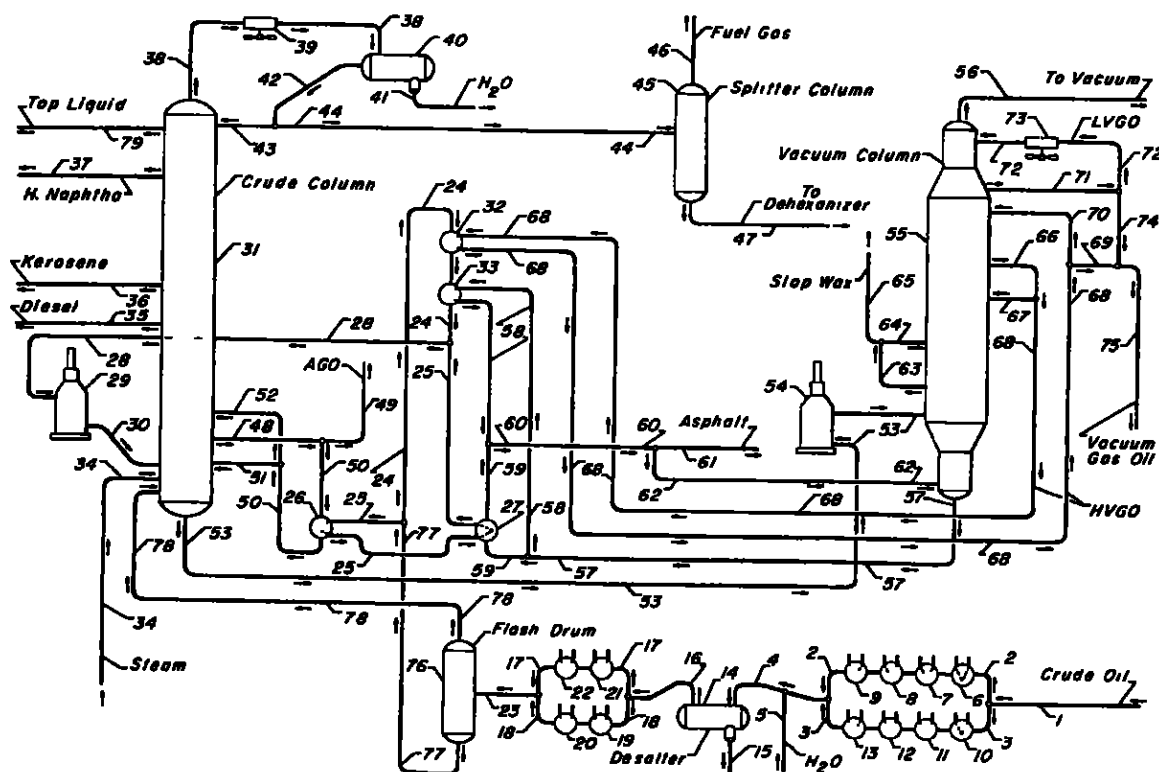
Primary Examiner—Herbert Levine

Attorney, Agent, or Firm—James R. Hostson Jr Robert
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[57] ABSTRACT

The amount of heat input required for the sequential fractionation of a crude oil in a crude column and a vacuum column is reduced by an improved heat exchange method wherein the desalted crude oil is flashed and the flash zone liquid is split into two streams. One of the streams is first heat exchanged against an atmospheric gas oil stream from the crude column and then against a first asphalt stream from the vacuum column. The other stream is first heat exchanged against a heavy vacuum gas oil stream from the vacuum column and then against a second asphalt stream from the vacuum column. The two streams are then recombined heated and passed into the crude column.

2 Claims, 1 Drawing Figure



INTEGRATED HEAT EXCHANGE ON CRUDE OIL AND VACUUM COLUMNS

FIELD OF THE INVENTION

The invention relates to a process for the separation of mineral oils by fractional distillation. It also relates to the methods of heat exchange used to heat a crude oil before it is inserted into a crude oil fractionation column. It more specifically relates to an integrated heat exchange system wherein the desalted crude oil to be charged to a crude column is heated in part by heat exchange against liquid streams removed from a vacuum column. Processes concerned with similar areas of the art are found in Classes 208-353 and 208 354

PRIOR ART

The fractionation of crude oil is probably the single most basic process used in the petroleum industry. Those skilled in the art are therefore well informed as to various apparatus designs and methods of operation for crude oil distillation. The crude oil is customarily charged into a crude oil column operated at a slight positive pressure to perform an initial separation. Due to various limits set on the operation of this column such as operation below the temperature at which significant thermoc cracking begins to occur the bottoms stream removed from such an atmospheric crude column contains a significant amount of valuable gas oils. This bottoms stream is therefore often subjected to further fractionation at a lower pressure and higher temperature in a column referred to as the vacuum column.

The basic principles of atmospheric and vacuum distillation of crude oils may be reviewed by such standard references as *Petroleum Refinery Engineering*, Nelson 4th Ed McGraw Hill Book Co New York 1958. A more specific example of integrated crude and vacuum columns appears in U.S. Pat. No. 3,301,778 (Cl. 208-355) issued to J. T. Cabbage. This reference illustrates several features which are employed in the subject process and in most crude oil fractionation operations. These features include the removal of liquid sidecuts including kerosene and diesel oil from the crude column. These sidecuts are passed into individual side cut strippers in which light ends are removed from the sidecut liquid for return to the crude column. A second common feature shown in this reference is the use of a pump-around loop to provide intercooling for the crude column. In this system a stream of hot liquid is removed from a tray within the column and cooled by passage through an indirect heat exchange means. Typically this heat is transferred into another liquid stream which it is desired to heat, such as a portion of the crude oil. The cooled liquid is then returned to the column at some point which is in relatively close vertical proximity to the point at which it is removed. It is normally returned about three or four trays above or below the draw-off point. In one mode of operation the hot liquid sidecut stream is divided into two portions, one of which is passed into a sidecut stripper, while the other one is passed into an intercooler heat exchanger and returned to the column. Pump-around loops are also normally employed on the vacuum column. The liquid sidecuts from the vacuum column may also be passed into side-cut strippers but this is a less common situation.

The energy input required to vaporize the liquids entering the crude and the vacuum columns has resulted

in a continuing effort to maximize the recovery of useful heat from various streams in these two columns. U.S. Pat. No. 3,819,511 (Cl. 208 353) issued to A. M. Peiser and M. J. DePasquale illustrates one method to reduce the utilities cost of operating a crude column. According to this method the raw crude is split into two parallel streams which are each heated by exchange against several streams desalted and then further heated by exchange before being combined and passed into the crude column. This illustrates that the prior art has recognized the principle of sequentially exchanging against successively hotter streams and that it may be advantageous to split the crude oil into two parallel streams to provide a more effective or efficient heat exchange system. The reference is however limited to atmospheric crude columns and does not indicate how the operation of the crude column may be beneficially integrated with a vacuum column.

U.S. Pat. No. 3,886,062 (Cl. 208 354) also issued to A. M. Peiser and M. J. DePasquale presents a three tower pressure-to vacuum distillation system featuring an integrated heat recovery system. In this rather complicated system the raw crude oil stream is first heat exchanged as an entity against three product streams and is then divided into two portions, one of which is exchanged in a pump-around loop while the other is exchanged against another product stream. The two portions are then reunited and exchanged against two pump-around loops and a fourth product stream before being passed into a desalter. The resultant desalted crude is heat exchanged against a product stream and split into two portions. One portion is heat exchanged against a pump-around loop on the pressurized crude column and then against the net residual bottoms product stream of the vacuum column. Another pump around loop, one of the product streams and finally against the total bottoms stream removed from the vacuum column. The other portion of heated desalted crude is heat exchanged against four different pump around loops and then re mixed with the first portion. This combined stream is then exchanged against the alop from the vacuum column and passed into the pressurized crude column. This reference differs in the use of three columns and in the method of heat exchange used. One example of this difference is the failure of the reference to teach the division of the vacuum column bottoms (asphalt) stream into two portions, each of which is heat exchanged against a separate portion of the desalted crude.

Other references describing various facets of crude oil fractionation are U.S. Pat. Nos. 3,798,153 (Cl. 208 48AA), 3,296,121 (Cl. 208 350), 3,338,825 (Cl. 208 350) and 3,320,159 (Cl. 208 363).

BRIEF SUMMARY OF THE INVENTION

The invention provides a process for fractionating crude oil utilizing both an atmospheric crude column and a vacuum crude column in which the net heat input to perform the fractionation is reduced. This process comprises dividing a warm flash zone liquid stream into two portions, one of which is further heated by heat exchange against a pump-around stream of atmospheric gas oil and then against a portion of the total asphalt stream removed from the bottom of the vacuum column. The other portion of flash zone liquid is heated by indirect exchange against a stream of heavy vacuum gas oil and then against the remaining portion of the total asphalt stream.

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DETAILED DESCRIPTION

In the fractionation of crude oils using both a crude column and a vacuum column it is necessary to vaporize a very high percentage of the crude oil stream and a sizable percentage of the crude column bottoms stream. This requires the expenditure of a large amount of energy. The cost of operating these columns and of obtaining the resultant petroleum derived products may therefore be lowered by performing the fractionation in a more energy efficient manner. One of the basic ways of recovering energy and improving the energy efficiency of a refining process is through expeditious heat exchange. It is the objective of this invention to provide a heat exchange method and a crude oil fractionation process which are highly energy efficient.

As used herein the terms crude column, crude oil column or crude oil fractionation column are intended to refer to a trayed fractional distillation column having means for the generation of reflux and for the vaporization of liquid removed from the bottom of the column for use within the column which is operated at a super atmospheric pressure below about 40 psig and to which a crude oil stream is charged. The terms vacuum column or crude oil vacuum column are intended to indicate a trayed fractionation column to which the net bottoms of a crude oil column is charged and which is operated at a subatmospheric pressure. Unless otherwise specified, all pressure indications refer to conditions at the top of the respective columns.

In describing the subject process it is necessary to refer to several multicomponent streams of hydrocarbonaceous liquids taken as sidecuts or bottoms streams from the columns. It is intended to adopt the customary definitions of those skilled in the art and classify these streams according to the location at which they are withdrawn from the respective fractionation column. The basic reason for this is that the boiling point ranges, as determined by the appropriate ASTM method, will vary depending on such factors as the crude oil composition, the capability of the column, the nature of the downstream processing units and the raw materials which it is desired to send to these units. In addition, the boiling point ranges of each stream may be affected by changes in operating conditions such as reflux ratio, pressure or temperature. The intended product slate and product specifications will also influence the boiling point ranges. Another possibility is that the columns may be provided with an alternative draw-off point to allow more flexibility in operation. It also is possible to adjust the initial boiling point (IBP) and end boiling point (EBP) etc. of many of the streams by the adjustment of the amount of intercooling performed at various points. For instance, the end point of the naphtha may be lowered. This has the effect of lowering the IBP of the kerosene sidecut stream and increasing its flow rate. Likewise, any change in the EBP of the kerosene results in a corresponding change in the diesel fuel make.

As used herein the term atmospheric gas oil (AGO) refers to a stream removed near the bottom of the crude oil column and which has the highest EBP of any stream removed from this column with the sole exception of the bottoms stream. A typical atmospheric gas oil has a boiling point range of from about 400° to about 650° F. The bottoms stream of the crude column is also referred to as a reduced crude or topped crude. It may

have an IBP of about 640° to 700° F and will contain over 1 wt. % of asphaltenes.

The term vacuum gas oil is intended to refer to the various sidecut streams which may be removed from a vacuum column. Normally two vacuum gas oil streams are removed from the vacuum column. The stream having a higher boiling point range and removed at a lower point in the column is referred to in the art as a heavy vacuum gas oil (HVGO). The stream removed above the HVGO drawoff is referred to as a light vacuum gas oil (LVGO). These two streams may be removed from the process as separate product streams or may be blended into a single product stream. A typical HVGO will have a boiling point range of from about 650° to about 1050° F and may be further characterized in that it contains less than about 0.3 wt. % asphaltenes. The vacuum gas oil streams are to be distinguished from a stream of heavy material which is removed near the bottom of the vacuum column and referred to as slop or slop wax. This stream is too viscous for use as fuel oil without being blended with a cut oil. However, it normally has a relatively low asphaltene content and is a suitable lube oil base stock after propane deasphalting. A typical slop wax has a gravity of about 11.0 to 16.5° API and an average molecular weight of about 580 to 620 or higher.

The bottoms stream of a vacuum column is referred to herein as an asphalt stream. This is because of the high asphaltene content of this material which ranges from about 2 to 20 wt. % and its essentially nondistillable character. These characteristics often relegate it to use as a bonding agent for aggregates to form paving material or for roof sealing. It may however be subjected to subsequent processing such as air blowing, propane deasphalting or coking etc. A vacuum column bottoms stream may be characterized as having an IBP above 1000° F, containing less than 50 vol. % distillable hydrocarbons and having a gravity of from about 1.0 to 8.5° API. The average molecular weight of the asphalt may be from about 700 to 900 or higher. Asphalt is sometimes referred to as pitch.

According to the preferred embodiment, the warm desalted crude oil is passed into a flash zone which separates it into a vapor stream and a liquid stream. This is a customary step in crude oil fractionation. Effective flashing conditions include a positive pressure less than that used in the previous heat exchange and preferably from about 10 to 30 psig and a temperature of from about 280° to 500° F or higher. Further details of the operations of desalting and flashing may be obtained by reference to U.S. Pat. No. 3,798,153 (Cl. 208-48AA).

The Drawing illustrates the preferred embodiment of the invention. The crude and vacuum units have a large number of lines carrying the various sidecuts and pump-around loops which have not been shown in order to more clearly present the inventive concept. Likewise, a large number of subsystems including controllers, valves, steam generators, fractionation trays, etc. have not been shown. These accouterments do not form part of the inventive concept and they may be any of the various types which are customarily used. This description of the drawing and the example given below are not intended to preclude the reasonable variation and modification of the disclosed invention as can be made by one skilled in the art.

Referring now to the Drawing, a stream of raw crude oil enters the process through line 1. This stream contains water removed from the desalter 14. It is split into

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two portions with the first portion traveling through line 2. The temperature of this first portion is increased by indirect heat exchange against a stream of crude column top pump-around liquid in heat exchanger 6, against a bottom stream from a kerosene sidecut stripper in exchanger 7 against the bottoms of a diesel oil sidecut stripper in exchanger 8 and finally against a kerosene sidecut stream which has previously been used to heat a stream of desalted crude oil. The second portion of the raw crude oil is passed through line 3. Its temperature is increased by heat exchange against the crude column top pump-around liquid in exchanger 10 and against the product draw (bottoms stream) removed from the heavy naphtha stripper in heat exchanger 11. It is then exchanged against a portion of the AGO product stream removed from the crude column in exchanger 12. Finally it is heated in exchanger 13 by a second portion of the same kerosene sidecut which is used in heat exchanger 9. The two portions of now heated crude oil are combined and passed into a first desalter which is not shown through line 4. A brine stream is rejected from the first desalter. A stream of water from line 5 is admixed with the crude oil removed from the first desalter and is passed into a second desalter 14. A water stream is removed in line 15 for admixture with the raw crude oil.

The desalted crude oil is removed from the second desalter in line 16 and divided into two portions. The portion of the desalted crude which passes through line 17 is heated by heat exchange against a first portion of a kerosene sidecut stream in heat exchanger 21 and then by a first portion of a diesel oil sidecut in heat exchanger 22. The portion of the desalted crude flows through line 18 is heated by a second portion of the kerosene sidecut in heat exchanger 19 and against a second portion of the diesel oil sidecut in heat exchanger 20. The two portions of desalted crude oil are then combined and passed through line 23 into a flash drum 76. Vapors from this flash drum are passed into the crude column via line 78.

The liquids remaining after the flashing operation are withdrawn in line 77 and divided into two portions with one portion passing through line 25 and a second portion passing through line 24. The flash drum liquid passing through line 25 is heat exchanged against a stream of AGO passing through line 50 in heat exchange means 26. It is then further increased in temperature by heat exchange against an asphalt stream passing through line 59 and heat exchange means 27. The other portion of flash drum liquid which is passing through line 24, is increased in temperature by heat exchange in exchanger 32 against a stream of HVGO passing through line 68 and then in heat exchange means 33 by indirect heat exchange against a stream of asphalt passing through line 58. The two portions of flash drum liquid in lines 24 and 25 are then admixed and passed through line 28 to a fired heater 29. The effluent of the heater is passed into the crude column 31 through line 30.

The crude column is operated under conditions effective to cause the separation of the crude oil into a bottoms stream removed in line 53, a stream of AGO removed in line 48, a diesel oil sidecut stream removed in line 35, kerosene removed in line 36, heavy naphtha removed in line 37 and overhead vapors removed in line 38. A top liquid stream is removed in line 79. This is a pump-around stream used to remove heat from the column and no part of the top liquid is withdrawn as a product. The sidecuts removed in lines 35, 36 and 37 are

passed to sidecut strippers which are not shown. The return lines carrying the overhead vapors of the sidecut strippers back to the crude column are also not shown as these are customary and well known in the art. Heat is recovered from these sidecut streams by heat exchange against the incoming crude oil in the manner previously described. Steam is added to the bottom of the crude column through line 34 to aid in the fractionation.

The overhead vapors of the crude column are passed through an overhead condenser 39. The resulting condensate stream is passed into overhead receiver 40 and separated into a hydrocarbon liquid phase and an aqueous phase. A water stream is removed from the overhead receiver in line 41. This is the water which is contained in the sidecut stripper overhead vapor streams and the steam added through line 34. A stream of light liquid hydrocarbons is removed from the receiver in line 42. A first portion of this stream is returned to the top of the crude column as reflux in line 43. This portion is admixed with top pump-around liquid which is used for heating the crude oil in heat exchangers 6 and 10 before entering the column. A second portion of the overhead liquid is passed through line 44 into a splitter column 45. The splitter column removes the C_3 hydrocarbons in line 46 for use as fuel gas or for passage to a gas concentration unit. The C_4+ portion of the overhead liquid is removed in line 47 and passed into a dehexanizer.

The AGO stream which is removed from the crude column in line 48 is divided into a product stream removed in line 49 and a pump-around stream which is passed through line 50. The hot AGO passing through line 50 is passed through the heat exchanger 26 to heat one of the two portions of flash drum liquid. It is then itself split into two portions and returned to the crude column at two separate vertical points through lines 51 and 52. The bottoms stream of the crude column is removed in line 53 and passed through a fired heater 54 before being inserted into the vacuum column 55.

The vacuum column is operated under conditions which are effective to separate the entering crude column bottoms stream into an overhead vapor stream removed in line 56, a stream of LVGO removed in line 71, a stream of HVGO removed in line 66, a stream of slop wax removed in line 63 and an asphalt bottoms stream removed in line 57. The asphalt bottoms stream is divided into a first portion passing through line 59 and a second portion passing through line 58. The asphalt stream passing through line 59 is used to heat the flash drum liquid in heat exchange means 27. The second asphalt stream passing through line 58 is used to heat a portion of the flash drum liquid in heat exchange means 33. The two asphalt streams are then combined and directed into line 60. A net asphalt stream is removed from the process in line 61 as a product stream while the remaining portion of asphalt is returned to the bottom of the vacuum column through line 62. The slop wax stream removed in line 63 is also divided into two portions. A first portion is not heat exchanged and is returned to the vacuum column in line 64. A second portion of the slop wax may be rejected through line 65 as a net product stream or may be admixed with the crude column bottoms stream carried by line 53. If removed as a product stream it may be blended with the asphalt stream removed from the process in line 61.

A portion of the HVGO which is removed from the vacuum column in line 66 is returned to the vacuum

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column in line 67 without passing through a heat exchanger. The remaining portion of the HVGO passes through line 68 to heat exchange means 32 where it is used to heat a portion of the flash drum liquid stream. It then flows through line 68 to the point at which it is bifurcated into a stream of HVGO returned to the vacuum column in line 70 and a stream of HVGO which is removed as a product stream in line 69. The stream of LVGO which is removed in line 71 is divided into a product stream removed in line 74 and a recycle stream passed through line 72. The LVGO recycle stream is cooled in an air cooler 73 and returned near the top of the vacuum column. The LVGO product stream in line 74 is blended with the HVGO product stream from line 69 to form a combined vacuum gas oil product stream removed from the process in line 75.

The preferred embodiment of the invention may be characterized as a process for fractionating a crude oil which comprises the steps of desalting a crude oil feed stream to form a desalted crude oil stream, heating the desalted crude oil stream by indirect heat exchange against a liquid stream removed as a side cut from a crude oil fractionation column dividing the desalted crude oil stream into a flash drum vapor stream and a flash zone liquid stream by passing the desalted crude oil stream into a flash zone operated at effective flashing conditions, passing the flash zone vapor stream into the crude oil fractionation column dividing the flash zone liquid stream into a first and a second aliquot portion having the same composition, heating the first aliquot portion of the flash zone liquid stream by indirect heat exchange against a heavy vacuum gas oil stream and then by indirect heat exchange against a first asphalt stream, heating the second aliquot portion of the flash zone liquid stream by indirect heat exchange against an atmospheric gas oil stream comprising hydrocarbonaceous liquid removed from the bottom one half of the crude oil fractionation column and then by indirect heat exchange against a second asphalt stream, recombining the first and second aliquot portions of the flash zone liquid stream and passing the flash zone liquid stream into the crude oil fractionation column after further heating the crude oil fractionation column being operated at conditions effective to separate the desalted crude oil stream into a crude column bottoms stream, the atmospheric gas oil stream and at least two other liquid sidecut streams having lower end boiling points than the atmospheric gas oil stream including a pressure above about 5 psig and a bottoms liquid temperature of from 500 to about 720° F, heating the crude column bottoms streams and passing the crude column bottoms stream into a crude oil vacuum column operated under conditions effective to separate the crude column bottoms stream into an asphalt bottoms stream, a heavy vacuum gas oil sidecut stream and a light vacuum gas oil sidecut stream, including a bottoms temperature of from about 650 to about 770° F and a pressure of less than one atmosphere absolute dividing the heavy vacuum gas oil sidecut stream into a first aliquot portion which is returned to the crude oil vacuum column and a second aliquot portion which is utilized as the heavy vacuum gas oil stream and then dividing the heavy vacuum gas oil stream into a first and a second aliquot portion after heat exchange against the first portion of the flash zone liquid stream with the first portion of the heavy vacuum gas oil stream also being returned to the crude oil vacuum column and the second portion being removed as a product and dividing

the asphalt bottoms stream into a first and a second aliquot portions and thereby forming the first and the second asphalt streams recombining the first and second asphalt streams after their respective heat exchange operations to form a cooled asphalt stream passing a first portion of the cooled asphalt stream into the crude oil vacuum column and removing a second portion of the cooled asphalt stream as a product.

The invention is further illustrated by this example of the preferred embodiment. The charge stream to the crude column is a 100,000 barrel per day (BPD) stream of a 34.5 API light Arabian crude oil. This stream is divided into two approximately equal portions. The first portion is admixed with about 4000 BPD of water from the second desalting stage and passed into heat exchanger 6 at about 95° F. It is heated to approximately 160° F by exchange against one part of the crude column top pump-around stream. This material is removed from a trap-out tray located between the third and fourth fractionation tray from the top of the column. Part of this material is returned to the crude column at the fourth tray and the remainder is admixed with the overhead liquid returned to the crude column as reflux. The crude oil is then heated to about 200° F by indirect heat exchange against the bottoms streams of the kerosene sidecut stripper in heat exchanger 7. In heat exchanger 8 the first portion of crude oil is further heated to 246° F by exchange against the bottom of the diesel oil sidecut stripper. It is then heated to 262° F in exchanger 9 by exchange against one portion of the kerosene sidecut which has previously been exchanged against a desalted crude stream in exchanger 19.

The second portion of raw crude is warmed from 95 to about 160° F in exchanger 10 against the remaining part of the previously described crude column top pump-around stream. It is then heated to close to 190° F by the bottoms stream of the naphtha sidecut stream. Exchange against the AGO product stream in heat exchanger 12 raises the temperature of this stream of raw crude to about 255° F. The temperature is finally raised to close to 269° F in exchanger 13 by exchange against the portion of the kerosene sidecut stream used for heating the desalted crude in exchanger 21. The two raw crude streams are mixed and passed into a first desalter from which undissolved water is decanted. A second stream of water is added to the crude before it is passed through a second desalter 14.

The now desalted crude is again split into two approximately equal parallel streams. Each stream is heated to about 317° and then to about 380° F by indirect contact with one part of the kerosene sidecut stream and then with one part of the diesel oil sidecut stream. The two streams of desalted crude are admixed and passed into a flash drum maintained at a pressure of about 15 psig. About 48,400 lbs./hr. of water vapor and gaseous hydrocarbons are removed from the flash drum and passed into the bottom of the crude column. This produces a 95,685 BPD stream of liquid hydrocarbons.

According to the inventive concept this liquid stream is split into two approximately equal portions. The first portion is heat exchanged against an HVGO stream in exchanger 32 to increase its temperature to about 495° F and against an asphalt stream in exchanger 33 to raise its temperature to about 515° F. The second portion of flash drum liquid is first heated to 505° F in heat exchanger 26 by the AGO pump-around stream and then to about 525° F by heat exchange against the other asphalt stream in exchanger 27. Admixture of the two

liquid streams produces a 520° F crude column feed stream which is charged into a fired heater. The mixed phase effluent of this heater has a temperature of about 712° F and a pressure of approximately 17 psig. It is charged directly into the crude column. About 15,900 lbs./hr. of 50 psig steam is also charged to the bottom of the crude column.

The streams removed from the crude column include a 38,100 BPD bottoms stream having a gravity of 15.9 API and a temperature of approximately 680° F. The total AGO sidcut stream has a temperature of about 575° F and a gravity of 30 API. The portion which is removed as a product stream in line 49 has a flow rate of 10,300 BPD and is heat exchanged against one of the streams of undesalted crude oil in exchanger 12. The remaining portion of the total AGO sidcut is exchanged against one of the streams of flash drum liquid and is thereby cooled to about 440° F. This portion is then split into two smaller streams and returned to the column in the manner illustrated.

The next lightest sidcut stream removed from the crude column is a 37.3 API diesel oil stream having a temperature of about 505° F. One portion of this sidcut is stripped with 50 psig steam with the resultant overhead vapors being returned to the crude column in the customary manner at a pressure of 13 psig. The bottoms stream of the stripper is exchanged against undesalted crude in exchanger 8 and removed at the rate of about 10,400 BPD. A second portion of the diesel oil sidcut is divided into three smaller streams. Two of these are used to heat the two streams of desalted crude in exchangers 20 and 22, and a smaller stream is used to reboil the naphtha stripper. The material forming these three streams is then returned to the crude column as the cooled part of the pump-around stream. In a similar manner a 410° F stream of kerosene is removed from the column and split into two portions. One portion is stripped with 50 psig steam to form a 12,000 BPD product stream having a gravity of 44 API. This stream is cooled from 390 to 210° F by raw crude oil in heat exchanger 7. Stripper overhead vapors are again returned to the column. A larger portion of the kerosene sidcut stream is divided into two streams which are passed in parallel through heat exchangers 19 and 21 and then through exchangers 9 and 13. These streams are then returned to the crude column at a lower temperature of about 300° F.

A heavy naphtha sidcut having a gravity of about 52.6 API is removed from the crude column at a temperature of 300° F. A first portion of this sidcut is passed into a reboiled stripper to produce a 12,000 BPD product stream having a temperature of 350° F. The naphtha product stream is then cooled to 210° F in heat exchanger 11. The remaining portion of the heavy naphtha sidcut is returned to the crude column at a point below the draw off tray at a temperature of 300° F. The top pump-around stream has a gravity of about 67.0° API and is removed at a temperature of 210° F. This stream is also split into two parallel streams which are cooled in heat exchangers 6 and 10 respectively. This top pump-around material has a temperature of about 145° F after the crude oil heat exchange and is returned to the column.

An overhead vapor stream is removed from the crude column at the rate of about 4,125 moles/hr. It has a temperature of 197° F and a pressure of 10 psig. This stream is cooled to about 100° F and passed into an overhead receiver. The hydrocarbon liquid phase col-

lected in the receiver has a gravity of about 76.3 API. A net overhead liquid is removed as a product stream passed into a dehexanizer at the rate of about 17,545 BPD. About 630 moles/hr. of overhead receiver liquid is returned to the column in admixture with a portion of the top pump-around stream as reflux. Water is decanted from the overhead receiver at the rate of approximately 1,540 moles/hr.

The bottoms stream of the crude column is heated to about 770° F and then flashed into the vacuum column at a pressure of 15 mm. of Hg absolute. An asphaltic bottoms stream having a gravity of 2 API is removed at a temperature of about 685° F. This total asphalt stream has a flow rate of approximately 205,500 lbs./hr. It is divided into two approximately equal smaller asphalt streams. The first asphalt stream is heat exchanged against flash drum liquid in heat exchanger 33 and the second asphalt stream is used to heat flash drum liquid in exchanger 27. The two streams are then recombined. A net asphalt product stream having a flow rate of about 162,500 lbs./hr. is withdrawn in line 61. The remaining portion of the asphalt stream is returned to the bottom of the vacuum column at a temperature of approximately 560° F.

An HVGO stream is removed from the crude column at 540° F. A first portion of this 11.9 API stream is returned to the vacuum column as shown. The remaining portion of the HVGO has a flow rate of approximately 736,500 lbs./hr. This HVGO stream is used to heat flash drum liquid in heat exchanger 32 and to generate steam. It is then divided into a net HVGO product stream of about 288,000 lbs./hr. and a recycle HVGO stream which is cooled to about 175° F and passed into the vacuum column. A 650° F stream of 15 API slop wax stream is withdrawn from the column and also split into two streams. The smaller of these streams is passed into the vacuum column heater and the larger stream is returned directly to the vacuum column. The LVGO is removed at the rate of about 411,000 lbs./hr. This material has a temperature of 200° F and a gravity of 28.7 API. A net LVGO product stream having a flow rate of about 81,800 lbs./hr. (6,350 BPD) is admixed with the net HVGO product stream. The remaining portion of the LVGO is cooled to about 100° F and passed into the top of the vacuum column. About 1,500 lbs./hr. gases having an average molecular weight of 36 is removed at the top of the column through use of jet ejectors developing a vacuum of about 5 mm. Hg absolute.

I claim as my invention

1. A process for fractionating a crude oil which comprises the steps of

- (a) desalting a crude oil feed stream to form a desalted crude oil stream
- (b) heating the desalted crude oil stream by indirect heat exchange against a liquid stream removed as a sidcut from a crude oil fractionation column
- (c) dividing the desalted crude oil stream into a flash zone vapor stream and a flash zone liquid stream by passing the desalted crude oil stream into a flash zone operated at effective flashing conditions
- (d) passing the flash zone vapor stream into the crude oil fractionation column
- (e) dividing the flash zone liquid stream into a first and a second aliquot portion having the same composition,
- (f) heating the first aliquot portion of the flash zone liquid stream by indirect heat exchange against a

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heavy vacuum gas oil stream and then by indirect
heat exchange against a first asphalt stream
(g) heating the second aliquot portion of the flash
zone liquid stream by indirect heat exchange
against an atmospheric gas oil stream comprising 5
hydrocarbonaceous liquid removed from the bot
tom one-half of the crude oil fractionation column
and then by indirect heat exchange against a sec-
ond asphalt stream
(h) recombining the first and second aliquot portions 10
of the flash zone liquid stream and passing the flash
zone liquid stream into the crude oil fractionation
column after heating the crude oil fractionation
column being operated at conditions effective to
separate the desalted crude oil stream into a crude 15
column bottoms stream the atmospheric gas oil
stream and at least two other liquid sidecut streams
having lower end boiling points than the atmo-
spheric gas oil stream, including a pressure above
about 5 psig and a bottoms liquid temperature of 20
from 500 to about 720 F
(i) heating the crude column bottoms streams and
passing the crude column bottoms stream into a
crude oil vacuum column operated under condi- 25
tions effective to separate the crude column bot-
toms stream into an asphalt bottoms stream a
heavy vacuum gas oil sidecut stream and a light
vacuum gas oil sidecut stream including a bottoms
temperature of from about 650 to about 770 F

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and a pressure of less than one atmosphere abso-
lute
(j) dividing the heavy vacuum gas oil sidecut stream
into a first aliquot portion which is returned un-
cooled to the crude oil vacuum column and a sec-
ond aliquot portion which is utilized as the heavy
vacuum gas oil stream of step (f) and then dividing
the heavy vacuum gas oil stream into a first and a
second aliquot portion after heat exchange against
the first portion of the flash zone liquid stream
with the first portion of the heavy vacuum gas oil
stream also being returned to the crude oil vacuum
column and the second portion being removed as a
product, and
(k) dividing the asphalt bottoms stream into a first and
a second aliquot portion and thereby forming the
first and the second asphalt streams recombining
the first and second asphalt streams after the re-
spective heat exchange operations of steps (f) and
(g) to form a cooled asphalt stream, passing a first
portion of the cooled asphalt stream into the crude
oil vacuum column and removing a second portion
of the cooled asphalt stream as a product.
2. The process of claim 1 further limited in that the
desalted crude oil stream is heated prior to passage into
the flash zone by heat exchange against a diesel oil
stream removed as a sidecut from the crude oil fraction-
ation column
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[54] PROCESS FOR HYDROCARBON CONVERSION

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June 23, 1975 Netherlands .. 7507484

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[52] U.S. Cl. 208/50; 208/61, 208/80; 208/86; 208/93

[58] Field of Search 208/68, 80, 93, 50
208/61

[56] References Cited

U S PATENT DOCUMENTS

3,281 350	10/1966	Codet et al.	208/80
3 671 419	6/1972	Ireland et al	208/93
3 775,293	11/1973	Watkins	208/80

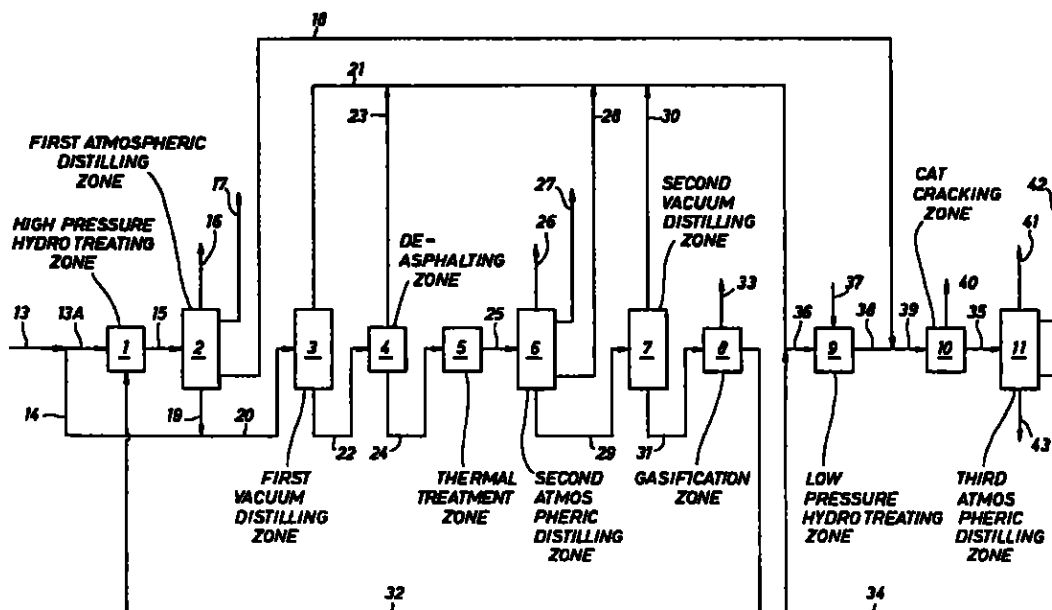
Primary Examiner—Herbert Levine

Attorney, Agent, or Firm—Ronald R. Reper

[57] **ABSTRACT**

Residual hydrocarbons stocks obtained after atmospheric distillation are converted into light distillates by certain sequences of processing steps including catalytic cracking, high and low pressure catalytic hydrotreatment, desasphalting, gasification and thermal cracking or coking

11 Claims, 6 Drawing Figures



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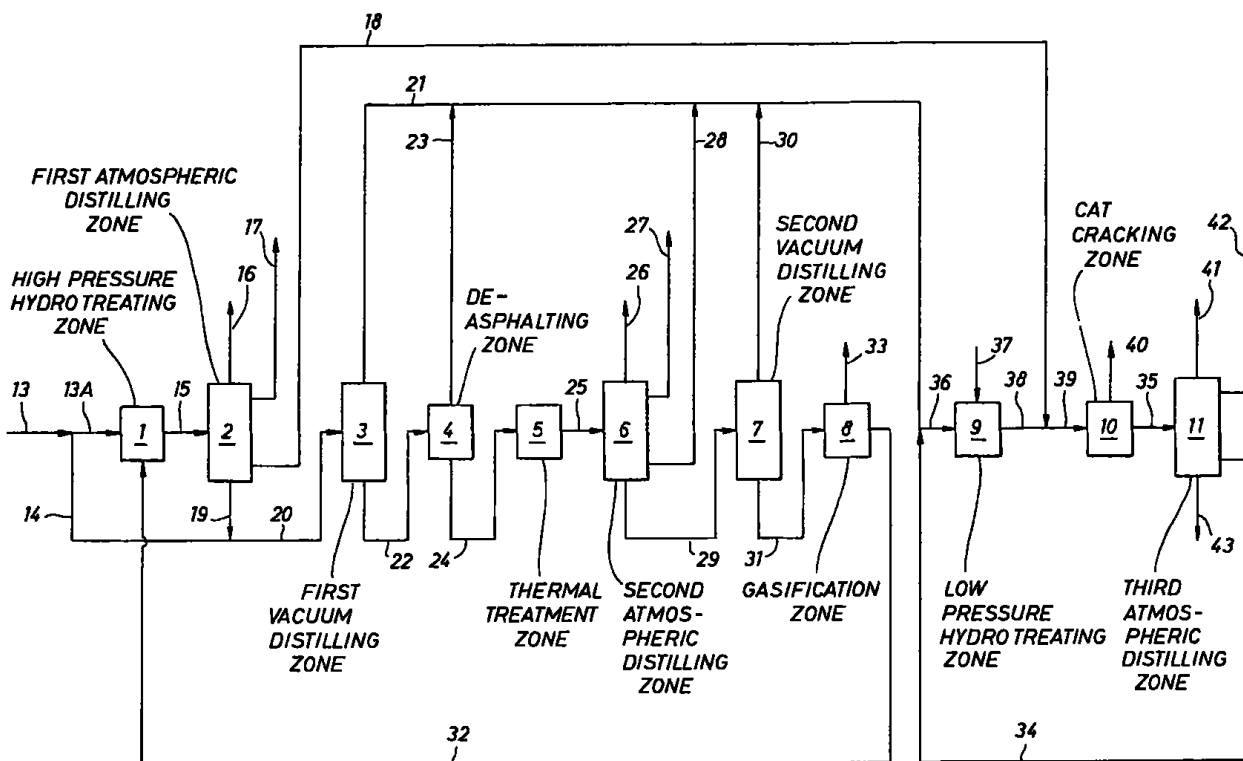


FIG 1

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FIG 2

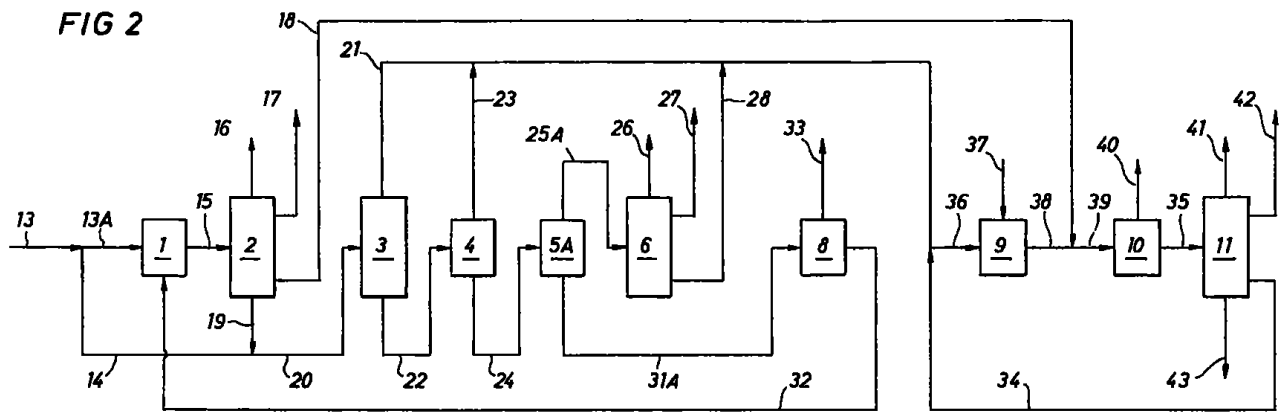


FIG 3

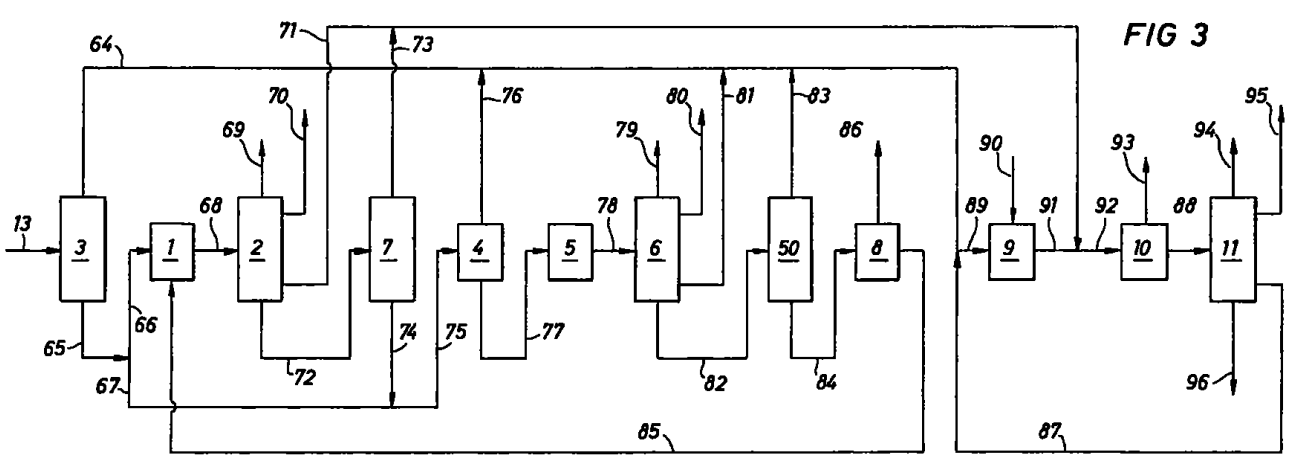


FIG 4

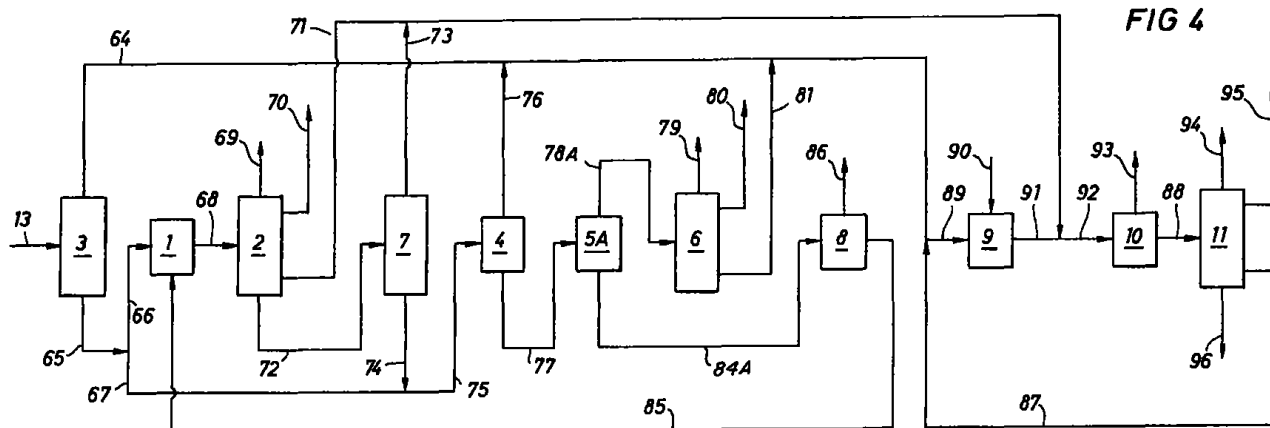
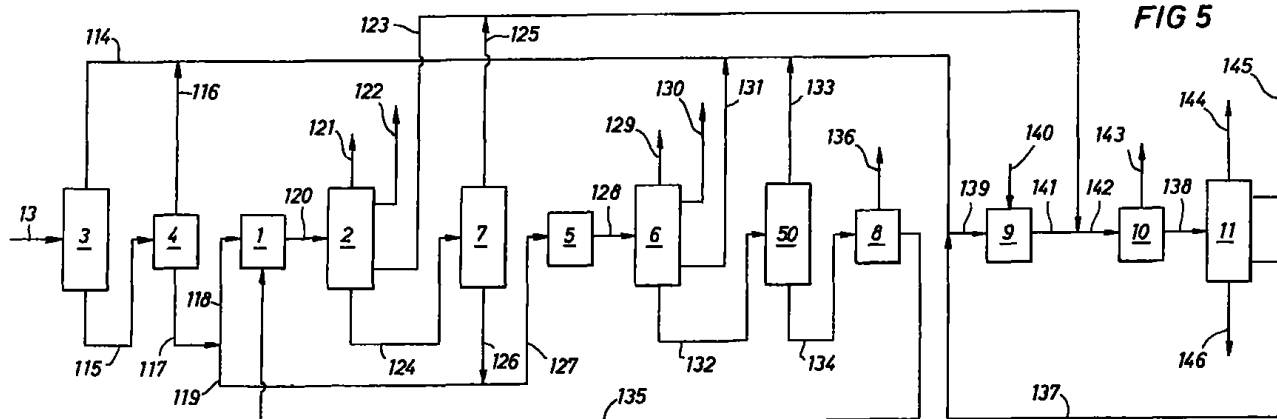


FIG 5



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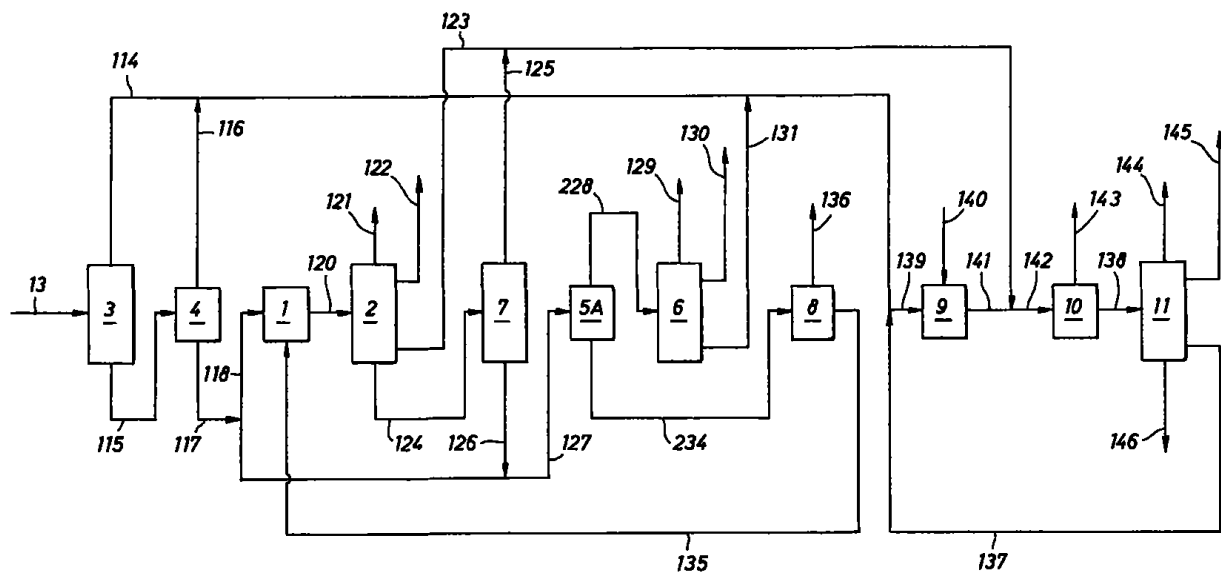


FIG 6

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PROCESS FOR HYDROCARBON CONVERSION

BACKGROUND OF THE INVENTION

The invention relates to a process for the production of one or more light hydrocarbon oil distillates from a hydrocarbon oil residue obtained by atmospheric distillation

During the atmospheric distillation of crude oil as employed on a large scale in the refineries for the production of light hydrocarbon oil distillates, a residual oil is obtained as a by product. In some cases this residual oil is suitable to serve as base i.e. starting material for the production of lubricating oil but often the residual oil which as a rule contains considerable quantities of sulfur metals and asphaltenes, only qualifies for use as fuel oil

In view of the growing need for light hydrocarbon oil distillates various processes have been proposed over the years which aimed at the conversion of the residual oils into light distillates. Exemplary processes include catalytic cracking thermal cracking gasification in combination with hydrocarbon synthesis coking and hydrocracking. The use of the residual oils as such as feed for each of these processes has considerable disadvantages which seriously hamper their application on a commercial scale. For instance the catalytic cracking of these residual oils has the serious drawbacks that catalyst consumption is very high and that owing to the high coke and gas production only a low yield of the desired light distillates is obtained. The thermal cracking of these residual oils for the production of light distillates is not attractive either because the stability of the cracked product permits only a low conversion to desired light distillates. Coking of the residual oils yields a considerable quantity of coke as product and this coke production occurs at the expense of the yield of desired light distillates. Gasification of the residual oils in combination with hydrocarbon synthesis is rather expensive and moreover not very attractive because in this way first the too heavy molecules are cracked to form too light molecules the latter subsequently being recombined to form heavier ones. The hydrocracking of the residual oils is accompanied by a rapid catalyst deactivation and/or a high production and/or a high consumption of hydrogen

In view of the above and taking into account the fact that in the atmospheric distillation of crude oil about half of the crude oil is left behind as distillation residue it will be clear that there is a pressing need for a process which offers the possibility of converting in an economically justifiable way hydrocarbon oil residues obtained by atmospheric distillation into light i.e. low boiling hydrocarbon oil distillates such as gasolines

As in practice catalytic cracking has proved to be an excellent process for the conversion of heavy hydrocarbon oil distillates such as gas oils into light hydrocarbon oil distillates such as gasolines the applicants have carried out an investigation in order to find out what use could be made of catalytic cracking for the conversion of hydrocarbon oil residues obtained by atmospheric distillation. It has been found that in a certain combination of catalytic cracking with catalytic high pressure hydrotreatment catalytic low pressure hydrotreatment, deasphalting gasification and thermal cracking or coking, a process can be realized which is highly suitable for this purpose. The present patent application relates to such a process

SUMMARY OF THE INVENTION

According to the invention there is provided a process for the production of light hydrocarbon distillates from a hydrocarbon oil residue obtained by atmospheric distillation which comprises

a fractionating said residue by vacuum distillation into a vacuum distillate and a vacuum residue

b deasphalting said vacuum residue in a deasphalting zone by contact with a low boiling hydrocarbon sorbent to obtain a deasphalted oil and asphalt

c catalytically cracking said vacuum distillate and said deasphalted oil in a catalytic cracking zone to obtain a catalytically cracked product,

d fractionating said catalytically cracked product by fractionation distillation at essentially atmospheric pressure to obtain at least one light hydrocarbon distillate product, and intermediate boiling fraction and a residue;

e hydrotreating said intermediate boiling fraction in a low pressure hydrotreating zone and recycling at least part of said intermediate fraction to said catalytic cracking zone

f thermally heating at least one of said asphalt and said residue in thermal treatment zone selected from a thermal cracking zone and a coking zone to obtain a thermal treatment product,

g fractionating said thermal product by fractionation distillation into at least one light distillate product a thermal intermediate fraction and a thermal residue,

h hydrotreating said thermal intermediate fraction in a low pressure hydrotreating zone and recycling at least part of this hydrotreated product as feed to the catalytic cracking zone,

i gasifying the thermal residual fraction in a gasification zone and catalytically reacting said gasified product with steam to produce hydrogen

j feeding said hydrogen to a high pressure catalytic hydrotreating zone together with at least part of the atmospheric distillation residue feed prior to step (a) or to at least part of the vacuum residue feed to step (b), then

k passing said hydrogen exiting said high pressure hydrotreating zone as feed to a low pressure catalytic hydrotreating zone together with a feed selected from the vacuum distillate product of step (a) and at least part of the asphalt product of step (b) and then

l passing said hydrogen exiting step (k) to at least one low pressure catalytic hydrotreating zone selected from steps (e) and (h)

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS 1 to 6 each illustrates different embodiments of the processing scheme according to the invention

DESCRIPTION OF PREFERRED EMBODIMENTS

In the process according to the invention a hydrocarbon oil residue obtained by atmospheric distillation (AR) and/or an atmospheric residue obtained therefrom by catalytic high pressure hydrotreatment and distillation of the hydrotreated product is split, by vacuum distillation into a vacuum distillate (VD) and a vacuum residue (VR). The vacuum residue and/or a vacuum residue obtained therefrom by catalytic high pressure hydrotreatment and distillation of the hydrotreated product, is split by deasphalting into a deasphalted oil and asphalt. The deasphalted oil and the vacuum distillate (VD) are cracked catalytically and

the cracked product is separated by atmospheric distillation into one or more light distillates as end products, an intermediate fraction of which at least a part is again cracked catalytically after a catalytic low pressure hydrotreatment, and a residue. The asphalt and/or a vacuum residue or asphalt fraction obtained therefrom by catalytic high pressure hydrotreatment and distillation or deasphalting, respectively of the hydrotreated product, is subjected to thermal cracking or coking and the product so obtained is split by distillation into one or more light distillates as end products, an intermediate fraction of which after a catalytic low pressure hydrotreatment is cracked catalytically and a residual fraction which is gasified for the production of hydrogen for the catalytic high pressure hydrotreatment. The last mentioned hydrotreatment is applied either to at least part of the atmospheric distillation residue (AR), or to at least part of the vacuum residue (VR) and is then combined with a catalytic low pressure hydrotreatment of the vacuum distillate (VD) or to at least part of the asphalt from the vacuum residue (VR) by deasphalting and is then combined with a catalytic low pressure hydrotreatment of both the vacuum distillate (VD) and the deasphalted oil.

In the process according to the invention catalytic cracking constitutes the main process. In the catalytic cracking operation a considerable part of the heavy feed is converted into desired light distillates. The cracked product is split by atmospheric distillation into one or more light distillates as end products, an intermediate fraction of which at least a part is again cracked catalytically after a catalytic low pressure hydrotreatment and a residue. Preferably more than 50%w of the intermediate fraction is subjected to a catalytic low pressure hydrotreatment followed by catalytic cracking. During catalytic cracking which is preferably carried out in the presence of a zeolite catalyst coke is deposited on the catalyst. This coke is removed from the catalyst by burning off during a catalyst regeneration that is combined with the catalytic cracking operation which produces a waste gas consisting substantially of a mixture of carbon monoxide and carbon dioxide. The catalytic cracking operation is preferably carried out at a temperature of from 400° to 550° C, a pressure of from 1 to 10 bar, a space velocity of from 0.25 to 4 kg feed per kg of catalyst per hour and a catalyst changing rate of from 0.1 to 5 tons of catalyst per 1000 tons of feed. Specially preferred conditions for carrying out the catalytic cracking operation include temperatures from about 450 to 525° C, pressures from about 1.5 to 7.5 bar, space velocities from about 0.5 to 2.5 kg kg⁻¹ hour⁻¹ and catalyst changing rates from about 0.2 to 2 tons of catalyst per 1000 tons of feed.

In the process according to the invention both a catalytic high pressure and a catalytic low pressure hydrotreatment are employed as supplementary processes. The two processes differ from each other primarily in that the hydrogen partial pressure employed in the high pressure treatment is always at least 25 bar higher than the one applied by the low pressure treatment. Preferably the difference between the two hydrogen partial pressures amounts to at least 50 bar. The catalytic high pressure hydrotreatment employed in the process is preferably carried out at a temperature of from 325 to 500° C, a hydrogen partial pressure of from 75 to 250 bar, a space velocity of from 0.1 to 2.5 l feed per catalyst per hour and a hydrogen/feed ratio of from 250-3000 NI/kg. Special preference exists for carrying

out the catalytic high pressure hydrotreatment at temperatures from about 350° to 475° C, hydrogen partial pressures from about 90 to 175 bar, space velocities from about 0.15 to 1.5 l¹¹⁶¹ hour⁻¹ and hydrogen/feed ratios from 300 to 2000 NI/kg. The catalytic low-pressure hydrotreatment employed in the process aims mainly at reducing the metal content of the feed for the catalytic cracking unit and thereby limiting the catalyst consumption in the cracking unit and further aims at saturating the feed for the catalytic cracking unit with hydrogen and thereby reducing coke deposition on the cracking catalyst and increasing the yield of desired product. The catalytic low pressure hydrotreatment is preferably carried out at a temperature of from 275 to 425° C, a hydrogen partial pressure of 20 to 75 bar, a space velocity of from 0.1 to 5 l feed per l of catalyst per hour and a hydrogen/feed ratio of from 100 to 2000 NI/kg. Specially preferred conditions for carrying out the catalytic low-pressure hydrotreatment include temperatures from about 300° to 400° C, hydrogen partial pressures from about 25 to 60 bar, space velocities from about 0.2 to 3 l¹¹⁶¹ hour⁻¹ and hydrogen/feed ratios from about 200 to 1500 NI/kg. Both in the high-pressure and in the low pressure hydrotreatment preferably a sulfided catalyst is used which contains nickel and/or cobalt and in addition molybdenum and/or tungsten on alumina, silica or silica-alumina as the carrier.

In the process according to the invention it is usual for the product obtained by catalytic high pressure hydrotreatment to be subjected in succession to an atmospheric and to a vacuum distillation. This yields one or more light distillates as end products, one or more heavier distillates as feed for the catalytic cracking unit and a vacuum residue. If the catalytic high pressure hydrotreatment is applied to asphalt the above-mentioned vacuum distillation of the atmospheric residue from the hydrotreated product may very suitably be replaced by deasphalting. The deasphalted oil obtained upon deasphalting of the atmospheric residue is used as a feed component for the catalytic cracking unit and the asphalt is subjected to thermal cracking or coking.

The process according to the invention further comprises a thermal cracking or coking step whereby a considerable proportion of the residual feed is converted into distillate. From this distillate a small quantity of light distillate can be isolated as end-product, however it consists substantially of heavier distillate which after a catalytic low pressure hydrotreatment is suitable to serve as a feed component for the catalytic cracking unit. The residual fraction which is left behind after working up of the product obtained by thermal cracking or coking serves as feed for the gasification zone. If in the process according to the invention thermal cracking is applied, this is preferably carried out at a temperature of from 400 to 525° C, a pressure of from 2.5 to 25 bar and a residence time of from 1 to 25 minutes. Special preference exists for carrying out the thermal cracking at a temperature of from 425 to 500° C, a pressure of from 5 to 20 bar and a residence time of from 5 to 20 minutes. If in the process according to the invention coking is employed this is preferably carried out at a temperature of from 400° to 600° C, a pressure of from 1 to 25 bar and a residence time of from 5 to 50 hours. Special preference exists for carrying out the coking at a temperature of from 425 to 550° C, a pressure of from 2.5 to 20 bar and a residence time of from 10 to 40 hours.

Finally, the process according to the invention comprises gasification as a supplementary process. As feed

for the gasification unit the residual fraction is used which is left behind after working up of the product obtained by thermal cracking or coking. The gasification is carried out by incomplete combustion of the feed with oxygen. Preferably steam is added to the mixture as moderator. In the incomplete combustion a crude gas is obtained consisting substantially of carbon monoxide and hydrogen and containing a considerable quantity of sulfur. The hydrogen content of this crude is increased by subjecting it to the water gas shift reaction in which carbon monoxide is converted into carbon dioxide and hydrogen by reaction with steam. The water gas shift reaction is preferably carried out by passing the gas to be converted at a temperature of between 325 and 400 C through two or more reactors containing a high temperature water gas shift catalyst and subsequently passing the partly converted gas mixture at a temperature of between 200 and 275 C through a reactor containing a low temperature water gas shift catalyst. As high-temperature water gas shift catalysts iron-chromium catalysts are very suitable. Effective low temperature water gas shift catalyst are copper-zinc catalysts. Each of the high and low temperature catalysts are preferably supported on a porous carrier such as alumina. In view of the rapid contamination of the catalysts by soot, this must, at least when use is made of conventional reactors, be removed from the gas before it is subjected to the catalytic water gas shift reaction. If use is made of sulfur-sensitive catalysts, such as the above-mentioned iron-chromium and copper-zinc catalysts, sulfur must also be removed from the gas before it is subjected to the catalytic water gas shift reaction. Removal of the sulfur from the crude gas may be omitted if use is made of sulfur insensitive catalysts such as the Ni/Mo/Al₂O₃ or Co/Mo/Al₂O₃ catalysts according to Dutch application 7394793 or the Ni/Mo/Al/Al₂O₃ or Co/Mo/Al/Al₂O₃ catalysts according to Dutch patent application 7305304. The water gas shift reaction is preferably carried out at a pressure of between 10 and 100 bar and in particular between 20 and 80 bar. The quantity of steam which is present in the gas mixture that is subjected to the water gas shift reaction preferably amounts to 1-50 mol per mol carbon monoxide. After completion of the water gas shift reaction hydrogen rich gas still has to be purified so as to obtain pure hydrogen. Insofar as removal of soot and sulfur has not already been effected prior to the water gas shift reaction it has to take place now. The purification of the hydrogen rich gas further comprises inter alia, the removal of the carbon dioxide formed and of unconverted carbon monoxide.

The hydrogen which in the process according to the invention is produced by gasification is primarily intended for use in the catalytic high pressure hydrotreatment. The process is preferably carried out in such a way that the quantity of hydrogen produced by gasification is at least sufficient to satisfy fully the hydrogen requirement of the catalytic high pressure hydrotreatment. If the gasification yields more hydrogen than is needed for the catalytic high pressure hydrotreatment the extra quantity of hydrogen may be used in the catalytic low pressure hydrotreatment or be used for an application beyond the scope of the process. The quantity of hydrogen obtained in the gasification is determined mainly by the quantity of feed which is supplied to the gasification section. The latter quantity can to a certain extent be controlled by variation of the conditions under which the catalytic high pressure hydrotreatment, the deasphalting and the thermal cracking or

coking are carried out. More effective means of controlling the quantity of feed which is offered to the gasification section are

- a. The use of part of the intermediate fraction and/or at least part of the residue from the catalytically cracked product as a feed component for the thermal cracking, coking or gasification,
- b. a repeated catalytic high pressure hydrotreatment of a heavy fraction of the product which has already undergone such a treatment
- c. application of the catalytic high pressure hydrotreatment to only a part of the eligible material instead of to all the material concerned and
- d. combinations of the measures mentioned under (a)-(c)

The present invention comprises a number of attractive variants using the measures mentioned under (a)-(c) above. These variants will be described briefly below and will partly be discussed in more detail by reference to the accompanying drawings.

Variant a) As described hereinbefore, the product obtained by catalytic cracking is split by atmospheric distillation into one or more light distillate fractions as end products, an intermediate fraction of which at least a part, after a catalytic low pressure hydrotreatment, is subjected once more to catalytic cracking and a residual fraction. According to variant a part of the intermediate fraction and/or at least part of the residue is employed as a feed component for the coker and/or gasification unit, and/or part of the intermediate fraction is employed as a feed component for the thermal cracker.

Variant b) As described hereinbefore the catalytic high pressure hydrotreatment is applied either to the atmospheric distillation residue that serves as feed for the process, or to the vacuum obtained therefrom by vacuum residue by deasphalting. According to variant b a part but less than 50%w of the atmospheric distillation residue or of the vacuum distillation residue or of the asphalt which is obtained upon splitting the hydrotreated product, is subjected once more to a catalytic high pressure hydrotreatment.

Variant c) With this variant only a part but more than 50%w of the atmospheric distillation residue which serves as feed for the process, or of the vacuum residue obtained therefrom by vacuum distillation, or of the asphalt obtained from the vacuum residue by deasphalting is subjected to high pressure catalytic hydrotreatment, the remainder being mixed with the hydrotreated product. When carrying out the process according to variant c it should be borne in mind that a number of the fractions eligible as feed for the catalytic cracking section contain components not previously subjected to a catalytic hydrotreatment. These fractions must therefore be subjected to a catalytic low pressure hydrotreatment prior to the catalytic cracking. Since in each of the three embodiments of the process according to the invention briefly described hereinbefore under variant c the asphalt and/or vacuum residue obtained therefrom by catalytic high pressure hydrotreatment and distillation of the hydrotreated product may be converted by thermal cracking or coking, these three embodiments correspond with six process schemes. These six process schemes will be explained in more detail below by reference to the accompanying drawings.

Process Scheme I (FIG. 1)

The process is carried out in a plant which comprises a catalytic high pressure hydrotreating zone 1, the first

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atmospheric distillation zone 2, the first vacuum distillation zone 3, a deasphalting zone 4, a thermal cracking zone 5, the second atmospheric distillation zone 6, the second vacuum distillation zone 7 a gasification zone 8 a catalytic low pressure hydrotreating zone 9 a catalytic cracking zone 10 and the third atmospheric distillation zone 11. A hydrocarbon oil residue 13 obtained by atmospheric distillation is divided into two portions 13A and 14. Residue portion 13A is subjected to a catalytic high pressure hydrotreatment and the hydrotreated product 15 is split by atmospheric distillation into a C_4 - fraction 16, a gasoline fraction 17, a middle distillate fraction 18 and a residue 19. The residue 19 is mixed with portion 14 of the atmospheric residue and the mixture 20 is split by vacuum distillation into a vacuum distillate 21 and a residue 22. The residue 22 is split by deasphalting into a deasphalted oil 23 and an asphalt 24. The asphalt 24 is thermally cracked and the thermally cracked product 25 is split by atmospheric distillation into a C_4 - fraction 26, a gasoline fraction 27, a middle distillate fraction 28 and a residue 29. The residue 29 is split by vacuum distillation into a vacuum distillate 30 and a residue 31. The residue 31 is gasified and the gas obtained is converted by means of the water gas shift reaction and purification, into hydrogen 32 which is fed to the catalytic high pressure hydrotreating unit and a waste gas 33 which substantially consists of carbon dioxide. The vacuum distillate 21, the deasphalted oil 23, the middle distillate fraction 28 and the vacuum distillate 30 are mixed with a middle distillate fraction 34, which is obtained by atmospheric distillation from the catalytically cracked product 35 still to be discussed and the mixture 36, together with a hydrogen stream supplied 37, is subjected to a catalytic low pressure hydrotreatment. The hydrotreated product 38 is mixed with the middle distillate fraction 18 and the mixture 39 is cracked catalytically. In the regeneration of the catalyst in the catalytic cracking unit a waste gas 40 is obtained which consists substantially of a mixture of carbon monoxide and carbon dioxide. The catalytically cracked product 35 is split by atmospheric distillation into a C_4 - fraction 41, a gasoline fraction 42 and a middle distillate fraction 34 and a residue 43.

Process Scheme II (FIG 2)

The process is carried out in a plant substantially like the one described under process scheme I and wherein the same numbers have the same meaning, the differences being that now instead of the thermal cracking zone 5, a coking zone 5A is present and that the second vacuum distillation zone 7 is omitted. The processing of the hydrocarbon oil residue 13A obtained by atmospheric distillation takes place in substantially the same way as described under process scheme I, the differences being that now instead of thermal cracking of the asphalt 24, coking of the asphalt is carried out to form a distillate 25A and coke 31A and that now instead of the vacuum residue 31 from the thermally cracked product the coke 31A is employed as feed for the gasification zone

Process Scheme III (FIG 3)

The process is carried out in a plant which comprises the first vacuum distillation zone 3, a catalytic high pressure hydrotreating zone 1, the first atmospheric distillation zone 2, the second vacuum distillation zone 7, a deasphalting zone 4, a thermal cracking zone 5 the second atmospheric distillation zone 6, the third vac-

uum distillation zone 50, a gasification zone 8, a catalytic low pressure hydrotreating zone 9, a catalytic cracking zone 10 and the third atmospheric distillation zone 11. A hydrocarbon oil residue 13 obtained by atmospheric distillation is split by vacuum distillation into a vacuum distillate 64 and a vacuum residue 65. The vacuum residue 65 is divided into two portions 66 and 67. Portion 66 is subjected to a catalytic high-pressure hydrotreatment and the hydrotreated product 68 is split by atmospheric distillation into a C_4 - fraction 69, a gasoline fraction 70, a middle distillate fraction 71 and a residue 72. The residue 72 is split by vacuum distillation into a vacuum distillate 73 and a residue 74. The residue 74 is mixed with portion 67 of the vacuum residue and the mixture 75 is split by deasphalting into a deasphalted oil 76 and an asphalt 77. The asphalt 77 is thermally cracked and the thermally cracked product 78 is split by atmospheric distillation into a C_4 - fraction 79, a gasoline fraction 80, a middle distillate fraction 81 and a residue 82. The residue 82 is split by vacuum distillation into a vacuum distillate 83 and a residue 84. The residue 84 is gasified and the gas obtained is converted by means of the water gas shift reaction and purification into hydrogen 85 which is fed to the catalytic high pressure hydrotreating unit and a waste gas 86 which substantially consists of carbon dioxide. The vacuum distillate 64, the deasphalted oil 76, the middle distillate fraction 71, the deasphalted oil 76, the middle distillate fraction 81 and the vacuum distillate 83 and are mixed with a middle distillate fraction 87, which is obtained by atmospheric distillation from the catalytically cracked product 88 still to be discussed and the mixture 89, together with a hydrogen stream supplied 90, is subjected to a catalytic low pressure hydrotreatment in zone 9. The hydrotreated product 91 is mixed with the middle distillate fraction 71 and the vacuum distillate 73 and the mixture 92 is cracked catalytically in catalytic cracking zone 10. In the regeneration of the catalyst in the catalytic cracking unit a waste gas 93 is obtained which substantially consists of a mixture of carbon monoxide and carbon dioxide. The catalytically cracked product 88 is split by atmospheric distillation in zone 11 into a C_4 - fraction 94, a gasoline fraction 95, a middle distillate fraction 87 and a residue 96.

Process Scheme IV

The process is carried out in a plant (FIG 4) which is substantially equal to the one described under process scheme III and in which the same numbers have the same meaning the differences being that now instead of the thermal cracking unit 5, a coking unit 5A is present and that the third vacuum distillation unit 50 is omitted. The processing of the hydrocarbon oil residue 13 obtained by atmospheric distillation takes place in substantially the same way as described under process scheme III the differences being that now instead of thermal cracking of the asphalt 77, coking of the asphalt is carried out to form a distillate 78A and coke 84A and that now instead of the vacuum residue 84 from the thermally cracked product, the coke 84A is employed as feed for the gasification unit

Process Scheme V

The process is carried out in a plant (FIG 5) which comprises the first vacuum distillation zone 3, a deasphalting zone 4, a catalytic high pressure hydrotreating zone 1, the first atmospheric distillation zone 2, the second vacuum distillation zone 7, a thermal cracking

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zone 5, the second atmospheric distillation unit 6, the third vacuum distillation unit 50, a gasification unit 8, a catalytic low pressure hydrotreating unit 9, a catalytic cracking unit 10 and the third atmospheric distillation unit 11. A hydrocarbon oil residue 13 obtained by atmospheric distillation is split by vacuum distillation into a vacuum distillate 114 and a residue 115. The residue 115 is split by deasphalting into a deasphalted oil 116 and an asphalt 117. The asphalt 117 is divided into two portions 118 and 119. Portion 118 is subjected to a catalytic high pressure hydrotreatment in zone 1 and the hydrotreated product 120 is split by atmospheric distillation into a C_4 - fraction and a residue 124. The residue 124 is split by vacuum distillation into a vacuum distillate 125 and residue 126. The residue 126 is mixed with portion 119 of the asphalt and the mixture 127 is thermally cracked. The thermally cracked product 128 is split by atmospheric distillation into a C_4 - fraction 129, a gasoline fraction 130, a middle distillate fraction 131 and a residue 132. The residue 132 is split by vacuum distillation into a vacuum distillate 133 and a residue 134. The residue 134 is gasified and the gas obtained is converted by means of the water gas shift reaction and purification into hydrogen 135 which is fed to the catalytic high-pressure hydrotreating unit and a waste gas 136 which substantially consists of carbon dioxide. The vacuum distillate 114, the deasphalted oil 116, the middle distillate 131 and the vacuum distillate 133 are mixed with a middle distillate fraction 137, which is obtained by atmospheric distillation from the catalytically cracked product 138 still to be discussed and the mixture 139, together with a hydrogen stream supplied 140, is subjected to a catalytic low pressure hydrotreatment. The hydrotreated product 141 is mixed with the middle distillate fraction 128 and the vacuum distillate 125 and the mixture 142 is cracked catalytically. In the regeneration of the catalyst in the catalytic cracking unit a waste gas 143 is obtained which substantially consists of a mixture of carbon monoxide and carbon dioxide. The catalytically cracked product 138 is split by atmospheric distillation into a C_4 - fraction 144, a gasoline fraction 145, a middle distillate fraction 137 and a residue 146.

Process Scheme VI

The process is carried out in a plant (FIG. 6) which is substantially equal to the one described under process scheme V and in which the same numbers have the same meaning the differences being that now instead of the thermal cracking unit 5, a coking unit 5A is present and that the third vacuum distillation unit 50 is omitted. The processing of the hydrocarbon oil residue 13 obtained by atmospheric distillation takes place in substantially the same way as described under process scheme V the differences being that now instead of thermal cracking of the mixture 127, coking of the mixture is carried out to form a distillate 228 and coke 234 and that now instead of the vacuum residue 134 of the thermally cracked product, the coke 234 is employed as feed for the gasification unit.

The present patent application also comprises plant for carrying out the process according to the invention as schematically represented in figures I-1-5.

The invention will now be elucidated by reference to the following examples.

The process according to the invention was applied to an atmospheric distillation residue from a crude oil originating from the Middle East. The atmospheric

distillation residue had an initial boiling point of 350° C, a sulfur content of 4%w and an asphaltene content of 18%w based upon C_4 and lighter (C_4 -) solvent. The process was carried out according to process schemes I-VI. In the various units the following conditions were employed.

With all process schemes for the catalytic high pressure hydrotreatment a sulfided cobalt molybdenum catalyst on alumina as the carrier was employed. When process schemes I and II were used the catalytic high-pressure hydrotreatment took place at an average temperature of 390° C, a hydrogen partial pressure of 100 bar, a space velocity of 0.75 kg oil per liter of catalyst per hour and a hydrogen/oil ratio of 1000 NI/kg. When process schemes III and IV were used the catalytic high pressure hydrotreatment took place at an average temperature of 390° C, a hydrogen partial pressure of 100 bar, a space velocity of 0.4 kg oil per liter of catalyst per hour and a hydrogen/oil ratio of 1000 NI/kg. When process schemes V and VI were used the catalytic high pressure hydrotreatment took place at an average temperature of 450° C, a hydrogen partial pressure of 150 bar, a space velocity of 0.2 kg oil per liter of catalyst per hour and a hydrogen/oil ratio of 1500 NI/kg.

With all process schemes deasphalting was carried out at 120° C with liquid butane as the solvent and using a solvent/oil weight ratio varying between 3.5:1 and 4.5:1.

When process schemes I, III and V were used thermal cracking was carried out at a pressure of 10 bar, a residence time to 15 minutes and a temperature varying between 450° and 470° C.

When process schemes II, IV and VI were used coking was carried out at a pressure of 3.5 bar, a temperature of 470° C and a residence time varying from 20 to 24 hours.

With all process schemes gasification was carried out at a temperature of 1300° C, a pressure of 30 bar, a steam/feed weight ratio of 0.8:1 and an oxygen/feed weight ratio of 0.8:1. The water gas shift reaction was carried out in succession in a high temperature zone over an iron-chromium catalyst at a temperature of 350° C and a pressure of 30 bar and in a low temperature zone over a copper-zinc catalyst at a temperature of 250° C and a pressure of 30 bar.

With all process schemes I-VI the catalytic low-pressure hydrotreatment was carried out at a hydrogen partial pressure of 35 bar, a space velocity of 0.5:1 oil per liter catalyst per hour, a hydrogen/oil ratio of 1000 NI/kg and a temperature varying from 375° to 385° C and using a sulfided nickel molybdenum catalyst on alumina as the carrier.

With all process schemes catalytic cracking was carried out at a temperature of 490° C, a pressure of 2.2 bar, a space velocity of 2 kg oil per kg catalyst per hour and a catalyst changing rate varying from 0.5 to 1.0 ton of catalyst per 1000 tons of oil and using a zeolite cracking catalyst.

EXAMPLE I

This example was carried out according to process scheme I. Starting from 126 parts by weight of the 350° C+ atmospheric distillation residue 12 the following quantities of the various streams were obtained:

100 parts by weight portion (13A),
26 parts by weight portion (14),
4.1 parts by weight C_4 - fraction (16),

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0.9 parts by weight C₇-200° C gasoline fraction (17),
 5.0 parts by weight 200°-350° C middle distillate fraction (18),
 91.3 parts by weight 350° C+ residue (19), 69.8 parts by weight 350°-520° C vacuum distillate (21), 47.5 parts by weight 520° C+ residue (22),
 37.0 parts by weight deasphalted oil (23),
 10.5 parts by weight asphalt (24),
 0.1 parts by weight C₄- fraction (26),
 0.8 parts by weight C₅ 200° C gasoline fraction (27),
 1.1 parts by weight 200°-350° C middle distillate fraction (28),
 8.5 parts by weight 350° C+ residue (29),
 1.5 parts by weight 350°-520° C vacuum distillate (30),
 7.0 parts by weight 520° C+ residue (31),
 1.3 parts by weight hydrogen (32),
 18.0 parts by weight 200°-350° C middle distillate fraction (34),
 28.0 parts by weight C₄- fraction (41),
 74.0 parts by weight C₅ 200° C gasoline fraction (42) and
 6.0 parts by weight 350° C+ residue (43)

EXAMPLE II

This example was carried out according to process scheme II. Starting from 148 parts by weight of the 350° C+ atmospheric distillation residue 12 the following quantities of the various streams were obtained:

100 parts by weight portion (13A),
 4.8 parts by weight portion (14),
 4.1 parts by weight C₄- fraction (16),
 0.9 parts by weight C₅ 200° C gasoline fraction (17),
 5.0 parts by weight 200°-350° C middle distillate fraction (18),
 91.3 parts by weight 350° C+ residue (19),
 79.0 parts by weight 350°-520° C vacuum distillate (21),
 60.0 parts by weight 520° C+ residue (22),
 45.5 parts by weight deasphalted oil (23),
 14.5 parts by weight asphalt (24),
 6.7 parts by weight distillate (25),
 7.8 parts by weight coke (231),
 1.8 parts by weight C₄-fraction (26),
 1.5 parts by weight C₅ 200° C gasoline fraction (27),
 3.4 parts by weight 200°-350° C middle distillate fraction (34),
 32.4 parts by weight C₄- fraction (41),
 83.9 parts by weight C₅ 200° C gasoline fraction (42) and
 7.0 parts by weight 350° C+ residue (43)

EXAMPLE III

This example was carried out according to process scheme III. Starting from 100 parts by weight of the 350° C+ atmospheric distillation residue 13 the following quantities of the various streams were obtained:

44.0 parts by weight 350°-520° C vacuum distillate (64),
 56.0 parts by weight 520° C+ residue (65),
 41.2 parts by weight portion (66),
 14.8 parts by weight portion (67),
 2.8 parts by weight C₄- fraction (69),
 2.3 parts by weight C₇-200° C gasoline fraction (70),
 5.8 parts by weight 200°-350° C middle distillate fraction (71),
 31.4 parts by weight 350° C+ residue (72),
 14.5 parts by weight 350°-520° C vacuum distillate (73),
 16.9 parts by weight 520° C residue (74),
 23.4 parts by weight deasphalted oil (76),

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8.3 parts by weight asphalt (77),
 0.1 parts by weight C₄- fraction (79),
 0.6 parts by weight C₅ 200° C gasoline fraction (80),
 0.8 parts by weight 200°-350° C middle distillate fraction (81),
 6.8 parts by weight 350° C+ residue (82),
 1.1 parts by weight hydrogen (85),
 14.6 parts by weight 200°-350° C middle distillate fraction (87),
 21.9 parts by weight C₄- fraction (94),
 56.5 parts by weight C₅-200° C gasoline fraction (95) and
 4.9 parts by weight 350° C+ residue (96).

EXAMPLE IV

This example was carried out according to process scheme IV. Starting from 100 parts by weight of the 350° C+ atmospheric distillation residue 13 the following quantities of the various streams were obtained:

44.0 parts by weight 350°-520° C vacuum distillate (64),
 56.0 parts by weight 520° C+ residue (65),
 34.0 parts by weight portion (66),
 22.0 parts by weight portion (67),
 2.2 parts by weight C₄- fraction (69),
 1.9 parts by weight C₇-200° C gasoline fraction (70),
 4.8 parts by weight 200°-350° C middle distillate fraction (71),
 25.9 parts by weight 350° C+ residue (72),
 12.0 parts by weight 350°-520° C vacuum distillate (73),
 13.9 parts by weight 520° C+ residue (74),
 26.5 parts by weight deasphalted oil (76),
 9.4 parts by weight asphalt (77),
 4.3 parts by weight distillate (78),
 5.1 parts by weight coke (84A),
 1.1 parts by weight C₄+ fraction (79),
 1.0 parts by weight C₅ 200° C gasoline fraction (80),
 2.2 parts by weight 200°-350° C middle distillate fraction (81),
 0.8 parts by weight hydrogen (85),
 14.5 parts by weight 200°-350° C middle distillate fraction (87),
 21.8 parts by weight C₄- fraction (94),
 56.5 parts by weight C₅ 200° C gasoline fraction (95) and
 4.9 parts by weight 350° C+ residue (96)

EXAMPLE V

This example was carried out according to process scheme V. Starting from 100 parts by weight of the 350° C+ atmospheric distillation residue 13 the following quantities of the various streams were obtained:

44.0 parts by weight 350°-520° C vacuum distillate (114),
 56.0 parts by weight 520° C+ residue (115),
 33.0 parts by weight deasphalted oil (116),
 23.0 parts by weight asphalt (117),
 19.0 parts by weight portion (118),
 4.0 parts by weight portion (119),
 2.5 parts by weight C₄- fraction (121),
 1.7 parts by weight C₅-200° C gasoline fraction (122),
 7.5 parts by weight 200°-350° C middle distillate fraction (123),
 8.3 parts by weight 350° C+ residue (124),
 4.3 parts by weight 350°-520° C vacuum distillate (125),
 4.0 parts by weight 520° C+ residue (126),
 0.1 parts by weight C₄ fraction (129),
 0.6 parts by weight C₇-200° C gasoline fraction (130),

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0.8 parts by weight 200–350° C middle distillate fraction (131),
 6.5 parts by weight 350° C+ residue (132),
 1.5 parts by weight 350–520° C vacuum distillate (133),
 5.0 parts by weight 520° C+ residue (134),
 1.0 parts by weight hydrogen (135),
 14.6 parts by weight 200–300° C middle distillate fraction (137),
 22.2 parts by weight C₄- fraction (144),
 57.5 parts by weight C₃ 200° C gasoline fraction (145) and
 4.9 parts by weight 350° C+ residue (146).

EXAMPLE VI

This example was carried out according to process scheme VI. Starting from 100 parts by weight of the 350° C+ atmospheric distillation residue 13 the following quantities of the various streams were obtained:

44.0 parts by weight 350–520° C vacuum distillate (114),
 56.0 parts by weight 520° C- residue (115),
 33.0 parts by weight deasphalted oil (116),
 23.0 parts by weight asphalt (117),
 15.0 parts by weight portion (118),
 8.0 parts by weight portion (119),
 2.0 parts by weight C₄- fraction (121),
 1.4 parts by weight C₃ 200° C gasoline fraction (122),
 6.5 parts by weight 200–350° C middle distillate fraction (123),
 5.8 parts by weight 350° C+ residue (124),
 3.0 parts by weight 350–520° C vacuum distillate (125),
 2.8 parts by weight 520° C+ residue (126),
 6.6 parts by weight distillate (228),
 4.2 parts by weight coke (234),
 1.4 parts by weight C₄- fraction (129),
 1.3 parts by weight C₃ 200° C gasoline fraction (130),
 3.9 parts by weight 200–350° C middle distillate fraction (131),
 0.7 parts by weight hydrogen (135),
 14.5 parts by weight 200–350° C middle distillate fraction (137),
 22.1 parts by weight C₄- fraction (144),
 57.0 parts by weight C₃ 200° C gasoline fraction (145) and
 4.8 parts by weight 350° C+ residue (146).

What is claimed is:

1. A process for the production of light hydrocarbon distillates from a hydrocarbon oil residue obtained by atmospheric distillation which comprises:

- a. fractionating said residue by vacuum distillation into a vacuum distillate and a vacuum residue,
- b. deasphalting said vacuum residue in a deasphalting zone by contact with a low boiling hydrocarbon sorbent to obtain a deasphalted oil and asphalt
- c. catalytically cracking said vacuum distillate and said deasphalted oil in a catalytic cracking zone to obtain a catalytically cracked product
- d. fractionating said catalytically cracked product by fractionation distillation at essentially atmospheric pressure to obtain at least one light hydrocarbon distillate product, an intermediate boiling fraction and a residue
- e. hydrotreating said intermediate boiling fraction in a low pressure hydrotreating zone and recycling at least part of said intermediate fraction to said catalytic cracking zone

- f. thermally heating at least one of said asphalt and said residue in thermal treatment zone comprising either a thermal cracking zone or a coking zone to obtain a thermal treatment product,
 - g. fractionating said thermal product by fractionation distillation into at least one light distillate product, a thermal intermediate fraction and a thermal residue,
 - h. hydrotreating said thermal intermediate fraction in a low pressure hydrotreating zone and recycling at least part of this hydrotreated product as feed to the catalytic cracking zone,
 - i. gasifying the thermal residual fraction in a gasification zone and catalytically reacting said gasified product with steam to produce hydrogen,
 - j. feeding said hydrogen to a high pressure catalytic hydrotreating zone together with at least part of the atmospheric distillation residue feed prior to step (a) or to at least part of the vacuum residue feed to step (b), then
 - k. passing said hydrogen exiting said high pressure hydrotreating zone as feed to a low pressure catalytic hydrotreating zone together with a feed selected from the vacuum distillate product of step (a) and at least part of the asphalt product of step (b) and then
 - l. passing said hydrogen exiting step (k) to at least one low pressure catalytic hydrotreating zone selected from steps (e) and (h)
2. A process according to claim 1 wherein in step (c) the catalytic cracking is carried out using a zeolite catalyst at a temperature of from 400 to 550° C, a pressure of from 1 to 10 bar, a space velocity of from 0.25 to 4 kg kg⁻¹ hour⁻¹ and a catalyst changing rate of from 0.1 to 5 tons of catalyst per 1000 tons of feed
3. A process according to claim 1 wherein the hydrogen partial pressure applied in the catalytic high pressure hydrotreating zone is at least 50 bar higher than the hydrogen partial pressure in the low-pressure hydrotreating zone.
4. A process according to claim 1 wherein the catalytic high pressure hydrotreatment is carried out using a sulfided catalyst which contains at least one of nickel and cobalt and in addition at least one of molybdenum and tungsten on a carrier selected from alumina, silica and silica-alumina, at a temperature of from about 325 to 500° C, a hydrogen partial pressure of from 90 to 175 bar, a space velocity of from 0.1 to 2.5 l l⁻¹ hour⁻¹ and a hydrogen/feed ratio of from 250 to 3000 Nl kg⁻¹
5. A process according to claim 1 wherein in steps (e) and (h) the catalytic low pressure hydrotreatment is carried out using a sulfided catalysts which contains at least one of nickel and cobalt and in addition at least one of molybdenum and tungsten on a carrier selected from alumina, silica or silica-alumina, at a temperature of from about 275 to 425° C, a hydrogen partial pressure of from 20 to 75 bar, a space velocity of from 0.1–5 l l⁻¹ hour⁻¹ and a hydrogen/feed ratio of from 100 to 2000 Nl kg⁻¹
6. A process according to claim 1 wherein in step (j) the feed to catalytic high pressure hydrotreatment is at least part of the asphalt obtained from step (b) and comprising the further steps of:
- fractionating the hydrotreated product of step (j) by fractionation distillation at essentially atmospheric pressure to obtain at least one light hydrocarbon distillate product, a middle distillate fraction and an atmospheric residue,

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passing said middle distillate fraction as a feed component to the catalytic cracking zone of step (c),
deasphalting said atmospheric residue in the deasphalting zone of step (b), to obtain a deasphalted oil and an asphalt
passing said deasphalted oil to a feed component to the catalytic cracking zone of step (c) and passing the asphalt to the thermal treatment zone of step (f)
7 A process according to claim 1 wherein in step (f) the thermal treatment comprises thermal cracking carried out at a temperature of from 400 to 525 C, a pressure of from 2.5 to 25 bar and a residence time of from 1 to 25 minutes.
8. A process according to claim 1 wherein in step (f) the thermal treatment comprises coking carried out at a temperature of from 400 to 600° C a pressure of from 1 to 25 bar and a residence time of from 5 to 50 hours.
9 A process according to claim 1 wherein in step (i) the gasification is carried out by incomplete combustion of the feed with air and in the presence of steam as

moderator the hydrogen content of the crude gas which consists substantially of carbon monoxide and hydrogen is increased by contacting the crude gas together with 1-50 mol steam per mol carbon monoxide at a pressure of from 10 to 100 bar in succession in a first zone with a high temperature water gas shift catalyst at a temperature from 325 to 400 C and then in a second zone with a low temperature water gas shift catalyst at a temperature from 200 to 275 C followed by purification of the hydrogen-rich gas thus obtained
10 A process according to claim 1 wherein at least one of (1) part of the intermediate boiling fraction product of step (d) and (2) at least part of the residue product of step (d) are passed as a feed component to the coking zone of step (f) or to the gasification zone of step (i)
11 A process according to claim 1 wherein part of the intermediate boiling fraction product of step (d) is passed as a feed component to the thermal cracking zone of step (f)
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