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(54) **INTEGRATED SOLVENT DEASPHALTING AND STEAM PYROLYSIS PROCESS FOR DIRECT PROCESSING OF A CRUDE OIL**

DEASPHALTIERUNGS- UND DAMPPYROLYSEVERFAHREN MIT INTEGRIERTEM
LÖSUNGSMITTEL ZUR DIREKTVERARBEITUNG VON ROHÖL

PROCÉDÉ INTÉGRÉ DE DÉSASPHALTAGE AU SOLVANT ET DE PYROLYSE À LA VAPEUR POUR
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Description

BACKGROUND OF THE INVENTION

5 Field of the Invention

[0001] The present invention relates to an integrated solvent deasphalting and steam pyrolysis process for direct processing of a crude oil to produce petrochemicals such as olefins and aromatics.

10 Description of Related Art

[0002] The lower olefins (i.e., ethylene, propylene, butylene and butadiene) and aromatics (i.e., benzene, toluene and xylene) are basic intermediates which are widely used in the petrochemical and chemical industries. Thermal cracking, or steam pyrolysis, is a major type of process for forming these materials, typically in the presence of steam, and in the absence of oxygen. Feedstocks for steam pyrolysis can include petroleum gases and distillates such as naphtha, kerosene and gas oil. The availability of these feedstocks is usually limited and requires costly and energy-intensive process steps in a crude oil refinery.

[0003] Studies have been conducted using heavy hydrocarbons as a feedstock for steam pyrolysis reactors. A major drawback in conventional heavy hydrocarbon pyrolysis operations is coke formation. For example, a steam cracking process for heavy liquid hydrocarbons is disclosed in United States Patent Number 4,217,204 in which a mist of molten salt is introduced into a steam cracking reaction zone in an effort to minimize coke formation. In one example using Arabian light crude oil having a Conradson carbon residue of 3.1% by weight, the cracking apparatus was able to continue operating for 624 hours in the presence of molten salt. In a comparative example without the addition of molten salt, the steam cracking reactor became clogged and inoperable after just 5 hours because of the formation of coke in the reactor.

[0004] In addition, the yields and distributions of olefins and aromatics using heavy hydrocarbons as a feedstock for a steam pyrolysis reactor are different than those using light hydrocarbon feedstocks. Heavy hydrocarbons have a higher content of aromatics than light hydrocarbons, as indicated by a higher Bureau of Mines Correlation Index (BMCI). BMCI is a measurement of aromaticity of a feedstock and is calculated as follows:

$$\text{BMCI} = 87552/\text{VAPB} + 473.5 * (\text{sp. gr.}) - 456.8 \quad (1)$$

where:

VAPB = Volume Average Boiling Point in degrees Rankine and
sp. gr. = specific gravity of the feedstock.

[0005] As the BMCI decreases, ethylene yields are expected to increase. Therefore, highly paraffinic or low aromatic feeds are usually preferred for steam pyrolysis to obtain higher yields of desired olefins and to avoid higher undesirable products and coke formation in the reactor coil section.

[0006] The absolute coke formation rates in a steam cracker have been reported by Cai et al., "Coke Formation in Steam Crackers for Ethylene Production," Chem. Eng. & Proc., vol. 41, (2002), 199 - 214. In general, the absolute coke formation rates are in the ascending order of olefins > aromatics > paraffins, wherein olefins represent heavy olefins.

[0007] To be able to respond to the growing demand of these petrochemicals, other type of feeds which can be made available in larger quantities, such as raw crude oil, are attractive to producers. Using crude oil feeds will minimize or eliminate the likelihood of the refinery being a bottleneck in the production of these petrochemicals. US 5 192 421 A teaches the solvent deasphalting of a whole crude.

[0008] While the steam pyrolysis process is well developed and suitable for its intended purposes, the choice of feedstocks has been very limited.

SUMMARY OF THE INVENTION

[0009] The system and process herein provides a steam pyrolysis zone integrated with a solvent deasphalting zone to permit direct processing of crude oil feedstocks to produce petrochemicals including olefins and aromatics.

[0010] The integrated solvent deasphalting and steam pyrolysis process for the direct processing of a crude oil to produce olefinic and aromatic petrochemicals comprises charging the crude oil to a solvent deasphalting zone with an effective amount of solvent to produce a deasphalted and demetalized oil stream and a bottom asphalt phase; thermally

cracking the deasphalted and demetalized oil stream in the presence of steam to produce a mixed product stream; separating the mixed product stream; recovering olefins and aromatics from the separated mixed product stream; and recovering pyrolysis fuel oil from the separated mixed product stream.

[0011] As used herein, the term "crude oil" is to be understood to include whole crude oil from conventional sources, crude oil that has undergone some pre-treatment. The term crude oil will also be understood to include that which has been subjected to water-oil separation; and/or gas-oil separation; and/or desalting; and/or stabilization.

[0012] Other aspects, embodiments, and advantages of the process of the present invention are discussed in detail below. Moreover, it is to be understood that both the foregoing information and the following detailed description are merely illustrative examples of various aspects and embodiments, and are intended to provide an overview or framework for understanding the nature and character of the claimed features and embodiments. The accompanying drawings are illustrative and are provided to further the understanding of the various aspects and embodiments of the process of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] The invention will be described in further detail below and with reference to the attached drawings where:

FIG. 1 is a process flow diagram of an embodiment of an integrated process described herein; and
FIGs. 2A-2C are schematic illustrations in perspective, top and side views of a vapor-liquid separation device used in certain embodiments of a steam pyrolysis unit in the integrated process described herein.

DETAILED DESCRIPTION OF THE INVENTION

[0014] A flow diagram including an integrated solvent deasphalting and steam pyrolysis process and system is shown in FIG. 1. The integrated system includes a solvent deasphalting zone, a steam pyrolysis zone 30 and a product separation zone.

[0015] Solvent deasphalting zone generally includes a primary settler 14, a secondary settler 17, a deasphalted/demetalized oil (DA/DMO) separation zone 20, and a separator zone 23.

[0016] Primary settler 14 includes an inlet for receiving a combined stream 13 including a feed stream 1 and a solvent, which can be fresh solvent 29, recycle solvent 12, recycle solvent 24, or a combination comprising one or more of these solvent sources. Primary settler 14 also includes an outlet for discharging a primary DA/DMO phase 15 and several pipe outlets for discharging a primary asphalt phase 16. Secondary settler 17 includes two tee-type distributors located at both ends for receiving the primary DA/DMO phase 15, an outlet for discharging a secondary DA/DMO phase 19, and an outlet for discharging a secondary asphalt phase 18. DA/DMO separation zone 20 includes an inlet for receiving secondary DA/DMO phase 19, an outlet for discharging a solvent stream 12 and an outlet for discharging a solvent-free DA/DMO stream 21 for use as the steam pyrolysis zone feedstock. Separator vessel 23 includes an inlet for receiving primary asphalt phase 16, an outlet for discharging a solvent stream 24, and an outlet for discharging a bottom asphalt phase 25.

[0017] Steam pyrolysis zone 30 generally comprises a convection section 32 and a pyrolysis section 34 that can operate based on steam pyrolysis unit operations known in the art, i.e., charging the thermal cracking feed to the convection section in the presence of steam. In addition, in certain optional embodiments as described herein (as indicated with dashed lines in FIG. 1), a vapor-liquid separation section 36 is included between sections 32 and 34. Vapor-liquid separation section 36, through which the heated steam cracking feed from the convection section 32 passes, can be a separation device based on physical or mechanical separation of vapors and liquids.

[0018] In one embodiment, a vapor-liquid separation device is illustrated by, and with reference to FIGs. 2A-2C. A similar arrangement of a vapor-liquid separation device is also described in U.S. Patent Publication Number 2011/0247500.

[0019] In this device vapor and liquid flow through is cyclonic geometry whereby the device operates isothermally and at very low residence time. In general vapor is swirled in a circular pattern to create forces where heavier droplets and liquid are captured and channeled through to a liquid outlet as low-sulfur fuel oil 38, for instance, which is added to a pyrolysis fuel oil blend, and vapor is channeled through a vapor outlet as the charge 37 to the pyrolysis section 34. The vaporization temperature and fluid velocity are varied to adjust the approximate temperature cutoff point, for instance in certain embodiments compatible with the residue fuel oil blend, e.g., about 540°C.

[0020] A quenching zone 40 includes an inlet in fluid communication with the outlet of steam pyrolysis zone 30, an inlet for admitting a quenching solution 42, an outlet for discharging the quenched mixed product stream 44 and an outlet for discharging quenching solution 46.

[0021] In general, an intermediate quenched mixed product stream 44 is converted into intermediate product stream 65 and hydrogen 62. Intermediate product stream 65 is generally fractionated into end-products and residue in separation

zone 70, which can one or multiple separation units such as plural fractionation towers including de-ethanizer, de-propanizer and de-butanizer towers, for example as is known to one of ordinary skill in the art. For example, suitable apparatus are described in "Ethylene," Ullmann's Encyclopedia of Industrial Chemistry, Volume 12, Pages 531 - 581, in particular Fig. 24, Fig 25 and Fig. 26.

[0022] In general the product separation zone 70 includes an inlet in fluid communication with the product stream 65, and plural product outlets 73-78, including an outlet 78 for discharging methane, an outlet 77 for discharging ethylene, an outlet 76 for discharging propylene, an outlet 75 for discharging butadiene, an outlet 74 for discharging mixed butylenes, and an outlet 73 for discharging pyrolysis gasoline. Additionally an outlet is provided for discharging pyrolysis fuel oil 71. The bottom asphalt phase 25 from separator vessel 23 and optionally the rejected portion 38 from vapor-liquid separation section 36 are combined with pyrolysis fuel oil 71 and the mixed stream can be withdrawn as a pyrolysis fuel oil blend 72, e.g., a low sulfur fuel oil blend to be further processed in an off-site refinery. Note that while six product outlets are shown, fewer or more can be provided depending, for instance, on the arrangement of separation units employed and the yield and distribution requirements.

[0023] In an embodiment of a process employing the arrangement shown in FIG. 1, a crude oil feedstock 1 is admixed with solvent from one or more of sources 29, 12 and 24. The resulting mixture 13 is then transferred to the primary settler 14. By mixing and settling, two phases are formed in the primary settler 14: a primary DA/DMO phase 15 and a primary asphalt phase 16. The temperature of the primary settler 14 is sufficiently low to recover all DA/DMO from the feedstock. For instance, for a system using n-butane a suitable temperature range is about 60°C to 150°C and a suitable pressure range is such that it is higher than the vapor pressure of n-butane at the operating temperature e.g. about 15 to 25 bars to maintain the solvent in liquid phase. In a system using n-pentane a suitable temperature range is about 60°C to about 180°C and again a suitable pressure range is such that it is higher than the vapor pressure of n-pentane at the operating temperature e.g. about 10 to 25 bars to maintain the solvent in liquid phase. The temperature in the second settler is usually higher than the one in the first settler.

[0024] The primary DA/DMO phase 15 including a majority of solvent and DA/DMO with a minor amount of asphalt is discharged via the outlet located at the top of the primary settler 14 and collector pipes (not shown). The primary asphalt phase 16, which contains 40-50 % by volume of solvent, is discharged via several pipe outlets located at the bottom of the primary settler 14.

[0025] The primary DA/DMO phase 15 enters into the two tee-type distributors at both ends of the secondary settler 17 which serves as the final stage for the extraction. A secondary asphalt phase 18 containing a small amount of solvent and DA/DMO is discharged from the secondary settler 17 and recycled back to the primary settler 14 to recover DA/DMO. A secondary DA/DMO phase 19 is obtained and passed to the DA/DMO separation zone 20 to obtain a solvent stream 12 and a solvent-free DA/DMO stream 21. Greater than 90 wt % of the solvent charged to the settlers enters the DA/DMO separation zone 20, which is dimensioned to permit a rapid and efficient flash separation of solvent from the DA/DMO. The primary asphalt phase 16 is conveyed to the separator vessel 23 for flash separation of a solvent stream 24 and a bottom asphalt phase 25. Solvent streams 12 and 24 can be used as solvent for the primary settler 14, therefore minimizing the fresh solvent 29 requirement.

[0026] The solvents used in solvent deasphalting zone include pure liquid hydrocarbons such as propane, butanes and pentanes, as well as their mixtures. The selection of solvents depends on the requirement of DAO, as well as the quality and quantity of the final products. The operating conditions for the solvent deasphalting zone include a temperature at or below critical point of the solvent; a solvent-to-oil ratio in the range of from 2:1 to 50:1; and a pressure in a range effective to maintain the solvent/feed mixture in the settlers is in the liquid state.

[0027] The essentially solvent-free DA/DMO stream 21 is optionally steam stripped (not shown) to remove any remaining solvent, and is the pyrolysis feedstream which is passed to the convection section 32 in the presence of an effective amount of steam, e.g., admitted via a steam inlet (not shown). In the convection section 32 the mixture is heated to a predetermined temperature, e.g., using one or more waste heat streams or other suitable heating arrangement. The heated mixture of the light fraction and steam is optionally passed to the vapor-liquid separation section 36 in which a portion 38 is rejected as a fuel oil component suitable for blending with pyrolysis fuel oil 71. The remaining hydrocarbon portion is conveyed to the pyrolysis section 34 to produce a thermally cracked mixed product stream 39.

[0028] The steam pyrolysis zone 30 operates under parameters effective to DA/DMO stream 21 into the desired products, including ethylene, propylene, butadiene, mixed butenes and pyrolysis gasoline. In certain embodiments, steam cracking is carried out using the following conditions: a temperature in the range of from 400°C to 900°C in the convection section and in the pyrolysis section; a steam-to-hydrocarbon ratio in the convection section in the range of from 0.3:1 to 2:1; and a residence time in the convection section and in the pyrolysis section in the range of from 0.05 seconds to 2 seconds.

[0029] In certain embodiments, the vapor-liquid separation section 36 includes one or a plurality of vapor liquid separation devices 80 as shown in FIGs. 2A-2C. The vapor liquid separation device 80 is economical to operate and maintenance free since it does not require power or chemical supplies. In general, device 80 comprises three ports including an inlet port for receiving a vapor-liquid mixture, a vapor outlet port and a liquid outlet port for discharging and

the collection of the separated vapor and liquid, respectively. Device 80 operates based on a combination of phenomena including conversion of the linear velocity of the incoming mixture into a rotational velocity by the global flow pre-rotational section, a controlled centrifugal effect to pre-separate the vapor from liquid (residue), and a cyclonic effect to promote separation of vapor from the liquid (residue). To attain these effects, device 80 includes a pre-rotational section 88, a controlled cyclonic vertical section 90 and a liquid collector/settling section 92.

[0030] As shown in FIG. 2B, the pre-rotational section 88 includes a controlled pre-rotational element between cross-section (S1) and cross-section (S2), and a connection element to the controlled cyclonic vertical section 90 and located between cross-section (S2) and cross-section (S3). The vapor liquid mixture coming from inlet 82 having a diameter (D1) enters the apparatus tangentially at the cross-section (S1). The area of the entry section (S1) for the incoming flow is at least 10% of the area of the inlet 82 according to the following equation:

$$\frac{\pi * ([D1])^2}{4} \quad (1)$$

[0031] The pre-rotational element 88 defines a curvilinear flow path, and is characterized by constant, decreasing or increasing cross-section from the inlet cross-section S1 to the outlet cross-section S2. The ratio between outlet cross-section from controlled pre-rotational element (S2) and the inlet cross-section (S1) is in certain embodiments in the range of $0.7 \leq S2/S1 \leq 1.4$.

[0032] The rotational velocity of the mixture is dependent on the radius of curvature (R1) of the center-line of the pre-rotational element 38 where the center-line is defined as a curvilinear line joining all the center points of successive cross-sectional surfaces of the pre-rotational element 88. In certain embodiments the radius of curvature (R1) is in the range of $2 \leq R1/D1 \leq 6$ with opening angle in the range of $150^\circ \leq \alpha R1 \leq 250^\circ$.

[0033] The cross-sectional shape at the inlet section S1, although depicted as generally square, can be a rectangle, a rounded rectangle, a circle, an oval, or other rectilinear, curvilinear or a combination of the aforementioned shapes. In certain embodiments, the shape of the cross-section along the curvilinear path of the pre-rotational element 38 through which the fluid passes progressively changes, for instance, from a generally square shape to a rectangular shape. The progressively changing cross-section of element 88 into a rectangular shape advantageously maximizes the opening area, thus allowing the gas to separate from the liquid mixture at an early stage and to attain a uniform velocity profile and minimize shear stresses in the fluid flow.

[0034] The fluid flow from the controlled pre-rotational element 88 from cross-section (S2) passes section (S3) through the connection element to the controlled cyclonic vertical section 40. The connection element includes an opening region that is open and connected to, or integral with, an inlet in the controlled cyclonic vertical section 90. The fluid flow enters the controlled cyclonic vertical section 90 at a high rotational velocity to generate the cyclonic effect. The ratio between connection element outlet cross-section (S3) and inlet cross-section (S2) in certain embodiments is in the range of $2 \leq S3/S1 \leq 5$.

[0035] The mixture at a high rotational velocity enters the cyclonic vertical section 90. Kinetic energy is decreased and the vapor separates from the liquid under the cyclonic effect. Cyclones form in the upper level 90a and the lower level 90b of the cyclonic vertical section 90. In the upper level 90a, the mixture is characterized by a high concentration of vapor, while in the lower level 90b the mixture is characterized by a high concentration of liquid.

[0036] In certain embodiments, the internal diameter D2 of the cyclonic vertical section 90 is within the range of $2 \leq D2/D1 \leq 5$ and can be constant along its height, the length (LU) of the upper portion 90a is in the range of $1.2 \leq LU/D2 \leq 3$, and the length (LL) of the lower portion 90b is in the range of $2 \leq LL/D2 \leq 5$.

[0037] The end of the cyclonic vertical section 90 proximate vapor outlet 34 is connected to a partially open release riser and connected to the pyrolysis section of the steam pyrolysis unit. The diameter (DV) of the partially open release is in certain embodiments in the range of $0.05 \leq DV/D2 \leq 0.4$.

[0038] Accordingly, in certain embodiments, and depending on the properties of the incoming mixture, a large volume fraction of the vapor therein exits device 80 from the outlet 84 through the partially open release pipe with a diameter DV. The liquid phase (e.g., residue) with a low or non-existent vapor concentration exits through a bottom portion of the cyclonic vertical section 90 having a cross-sectional area S4, and is collected in the liquid collector and settling pipe 92.

[0039] The connection area between the cyclonic vertical section 90 and the liquid collector and settling pipe 92 has an angle in certain embodiment of 90° . In certain embodiments the internal diameter of the liquid collector and settling pipe 92 is in the range of $2 \leq D3/D1 \leq 4$ and is constant across the pipe length, and the length (LH) of the liquid collector and settling pipe 92 is in the range of $1.2 \leq LH/D3 \leq 5$. The liquid with low vapor volume fraction is removed from the apparatus through pipe 86 having a diameter of DL, which in certain embodiments is in the range of $0.05 \leq DL/D3 \leq 0.4$ and located at the bottom or proximate the bottom of the settling pipe

[0040] While the various members are described separately and with separate portions, it will be understood by one of ordinary skill in the art that apparatus 80 can be formed as a monolithic structure, e.g., it can be cast or molded, or it can be assembled from separate parts, e.g., by welding or otherwise attaching separate components together which may or may not correspond precisely to the members and portions described herein.

[0041] It will be appreciated that although various dimensions are set forth as diameters, these values can also be equivalent effective diameters in embodiments in which the components parts are not cylindrical.

[0042] Mixed product stream 39 is passed to the inlet of quenching zone 40 with a quenching solution 42 (e.g., water and/or pyrolysis fuel oil) introduced via a separate inlet to produce a quenched mixed product stream 44 having a reduced temperature, e.g., of about 300°C, and spent quenching solution 46 is discharged.

[0043] The gas mixture effluent 39 from the cracker is typically a mixture of hydrogen, methane, hydrocarbons, carbon dioxide and hydrogen sulfide. After cooling with water or oil quench, mixture 44 is compressed in a multi-stage compressor zone 51, typically in 4-6 stages to produce a compressed gas mixture 52. The compressed gas mixture 52 is treated in a caustic treatment unit 53 to produce a gas mixture 54 depleted of hydrogen sulfide and carbon dioxide. The gas mixture 54 is further compressed in a compressor zone 55, and the resulting cracked gas 56 typically undergoes a cryogenic treatment in unit 57 to be dehydrated, and is further dried by use of molecular sieves.

[0044] The cold cracked gas stream 58 from unit 57 is passed to a de-methanizer tower 59, from which an overhead stream 60 is produced containing hydrogen and methane from the cracked gas stream. The bottoms stream 65 from de-methanizer tower 59 is then sent for further processing in product separation zone 70, comprising fractionation towers including de-ethanizer, de-propanizer and de-butanizer towers. Process configurations with a different sequence of de-methanizer, de-ethanizer, de-propanizer and de-butanizer can also be employed.

[0045] According to the processes herein, after separation from methane at the de-methanizer tower 59 and hydrogen recovery in unit 61, hydrogen 62 having a purity of typically 80-95 vol% is obtained, which can be further purified as needed or combined with other off gases in the refinery. In addition, a portion of hydrogen from stream 62 can be utilized for the hydrogenation reactions of acetylene, methylacetylene and propadienes (not shown). In addition, according to the processes herein, methane stream 63 can optionally be recycled to the steam cracker to be used as fuel for burners and/or heaters.

[0046] The bottoms stream 65 from de-methanizer tower 59 is conveyed to the inlet of product separation zone 70 to be separated into product streams methane, ethylene, propylene, butadiene, mixed butylenes and pyrolysis gasoline discharged via outlets 78, 77, 76, 75, 74 and 73, respectively. Pyrolysis gasoline generally includes C5-C9 hydrocarbons, and benzene, toluene and xylenes can be extracted from this cut. Optionally one or both of the bottom asphalt phase 25 and the unvaporized heavy liquid fraction 38 from the vapor-liquid separation section 36 are combined with pyrolysis fuel oil 71 (e.g., materials boiling at a temperature higher than the boiling point of the lowest boiling C10 compound, known as a "C10+" stream) and the mixed stream can be withdrawn as a pyrolysis fuel oil blend 16, e.g., to be further processed in an off-site refinery (not shown). In certain embodiments, the bottom asphalt phase 25 can be sent to an asphalt stripper (not shown) where any remaining solvent is stripped-off, e.g., by steam.

[0047] Solvent deasphalting is a unique separation process in which residue is separated by molecular weight (density), instead of by boiling point, as in the vacuum distillation process. The solvent deasphalting process thus produces a low-contaminant deasphalted oil (DAO) rich in paraffinic type molecules, consequently decreases the BMCI as compared to the initial feedstock or a hydroprocessed feedstock.

[0048] Solvent deasphalting is usually carried out with paraffin streams having carbon number ranging from 3-7, in certain embodiments ranging from 4-5, and below the critical conditions of the solvent. Table 1 lists the properties of commonly used solvents in solvent deasphalting.

Table 1. Properties Of Commonly Used Solvents In Solvent Deasphalting

Name	Formula	MW g/g-mol	Boiling Point °C	Specific Gravity	Critical Temperature °C	Critical Pressure bar
propane	C ₃ H ₈	44.1	-42.1	0.508	96.8	42.5
n-butane	C ₄ H ₁₀	58.1	-0.5	0.585	152.1	37.9
i-butane	C ₄ H ₁₀	58.1	-11.7	0.563	135.0	36.5
n-pentane	C ₅ H ₁₂	72.2	36.1	0.631	196.7	33.8
i-pentane	C ₅ H ₁₂	72.2	27.9	0.625	187.3	33.8

[0049] The feed is mixed with a light paraffinic solvent with carbon numbers ranging 3-7, where the deasphalted oil is solubilized in the solvent. The insoluble pitch will precipitate out of the mixed solution and is separated from the DAO

phase (solvent-DAO mixture) in the extractor.

[0050] Solvent deasphalting is carried-out in liquid phase and therefore the temperature and pressure are set accordingly. There are two stages for phase separation in solvent deasphalting. In the first separation stage, the temperature is maintained lower than that of the second stage to separate the bulk of the asphaltenes. The second stage temperature is maintained to control the deasphalted / demetalized oil (DA/DMO) quality and quantity. The temperature has big impact on the quality and quantity of DA/DMO. An extraction temperature increase will result in a decrease in deasphalted / demetalized oil yield, which means that the DA/DMO will be lighter, less viscous, and contain less metals, asphaltenes, sulfur, and nitrogen. A temperature decrease will have the opposite effects. In general, the DA/DMO yield decreases having higher quality by raising extraction system temperature and increases having lower quality by lowering extraction system temperature.

[0051] The composition of the solvent is an important process variable. The solubility of the solvent increases with increasing critical temperature, generally according to $C_3 < iC_4 < nC_4 < iC_5$. An increase in critical temperature of the solvent increases the DA/DMO yield. However, it should be noted that the solvent having the lower critical temperature has less selectivity resulting in lower DA/DMO quality.

[0052] The volumetric ratio of the solvent to the solvent deasphalting unit charge impacts selectivity and to a lesser degree on the DA/DMO yield. Higher solvent-to-oil ratios result in a higher quality of the DA/DMO for a fixed DA/DMO yield. Higher solvent-to-oil ratio is desirable due to better selectivity, but can result in increased operating costs thereby the solvent-to-oil ratio is often limited to a narrow range. The composition of the solvent will also help to establish the required solvent to oil ratios. The required solvent to oil ratio decreases as the critical solvent temperature increases. The solvent to oil ratio is, therefore, a function of desired selectivity, operation costs and solvent composition.

[0053] The method and system herein provides improvements over known steam pyrolysis cracking processes:

use of crude oil as a feedstock to produce petrochemicals such as olefins and aromatics;
the hydrogen content of the feed to the steam pyrolysis zone is enriched for high yield of olefins;
in certain embodiments coke precursors are significantly removed from the initial whole crude oil which allows a decreased coke formation in the radiant coil; and
in certain embodiments additional impurities such as metals, sulfur and nitrogen compounds are also significantly removed from the starting feed which avoids post treatments of the final products.

[0054] The method and system of the present invention have been described above and in the attached drawings; however, modifications will be apparent to those of ordinary skill in the art and the scope of protection for the invention is to be defined by the claims that follow.

Claims

1. An integrated solvent deasphalting and steam pyrolysis process for the direct processing of a crude oil to produce olefinic and aromatic petrochemicals, the process comprising:

- a. charging the crude oil to a solvent deasphalting zone with an effective amount of solvent to produce a deasphalted and demetalized oil stream and a bottom asphalt phase;
- b. thermally cracking the deasphalted and demetalized oil stream in the presence of steam to produce a mixed product stream;
- c. separating the thermally cracked mixed product stream;
- d. recovering olefins and aromatics from the separated mixed product stream; and
- e. recovering pyrolysis fuel oil from the separated mixed product stream.

2. The integrated process of claim 1, wherein step (c) comprises

- compressing the thermally cracked mixed product stream with plural compression stages;
- subjecting the compressed thermally cracked mixed product stream to caustic treatment to produce a thermally cracked mixed product stream with a reduced content of hydrogen sulfide and carbon dioxide;
- compressing the thermally cracked mixed product stream with a reduced content of hydrogen sulfide and carbon dioxide;
- dehydrating the compressed thermally cracked mixed product stream with a reduced content of hydrogen sulfide and carbon dioxide;
- recovering hydrogen from the dehydrated compressed thermally cracked mixed product stream with a reduced content of hydrogen sulfide and carbon dioxide; and

obtaining olefins and aromatics as in step (d) and pyrolysis fuel oil as in step (e) from the remainder of the dehydrated compressed thermally cracked mixed product stream with a reduced content of hydrogen sulfide and carbon dioxide.

- 5 3. The integrated process of claim 2, further comprising separately recovering methane from the dehydrated compressed thermally cracked mixed product stream with a reduced content of hydrogen sulfide and carbon dioxide for use as fuel for burners and/or heaters in the thermal cracking step.
- 10 4. The integrated process of claim 1 wherein the thermal cracking step comprises heating the deasphalted and demetalized oil stream in a convection section of a steam pyrolysis zone, separating the heated deasphalted and demetalized oil stream into a vapor fraction and a liquid fraction, passing the vapor fraction to a pyrolysis section of a steam pyrolysis zone, and discharging the liquid fraction.
- 15 5. The integrated process of claim 4 wherein the discharged liquid fraction is blended with pyrolysis fuel oil recovered in step (e).
- 20 6. The integrated process of claim 4 wherein separating the heated deasphalted and demetalized oil stream into a vapor fraction and a liquid fraction is with a vapor-liquid separation device based on physical and mechanical separation.
- 25 7. The integrated process of claim 6 wherein the vapor-liquid separation device includes
a pre-rotational element having an entry portion and a transition portion, the entry portion having an inlet for receiving the flowing fluid mixture and a curvilinear conduit,
a controlled cyclonic section having
an inlet adjoined to the pre-rotational element through convergence of the curvilinear conduit and the cyclonic section,
a riser section at an upper end of the cyclonic member through which vapors pass;
30 and
a liquid collector/settling section through which liquid passes.
- 35 8. The integrated process of claim 1, wherein step (a) comprises
mixing the crude oil feedstock with make-up solvent and optionally fresh solvent;
transferring the mixture to a primary settler in which a primary deasphalted and demetalized oil phase and a primary asphalt phase are formed;
transferring the primary deasphalted and demetalized oil phase to a secondary settler in which a secondary deasphalted and demetalized oil phase and a secondary asphalt phase are formed;
40 recycling the secondary asphalt phase to the primary settler to recover additional deasphalted and demetalized oil;
conveying the secondary deasphalted and demetalized oil phase to a deasphalted and demetalized oil separation zone to obtain a recycle solvent stream and a substantially solvent-free deasphalted and demetalized oil stream;
conveying the primary asphalt phase is conveyed to a separator vessel for flash separation of an additional recycle solvent stream and a bottom asphalt phase,
45 wherein the substantially solvent-free deasphalted and demetalized oil stream is the feed to the steam pyrolysis zone.
- 50 9. The integrated process as in claim 8, wherein the bottom asphalt phase is blended with pyrolysis fuel oil recovered in step (e).

Patentansprüche

- 55 1. Integrierter Lösemitteldeasphaltierungs- und Dampfpyrolyseprozess für die direkte Verarbeitung von Rohöl, um olefinische und aromatische Erdölchemikalien zu erzeugen, wobei der Prozess umfasst, dass:
a. das Rohöl in eine Lösemitteldeasphaltierungszone mit einer effektiven Menge an Lösemittel geladen wird, um einen deasphaltierten und demetallisierten Ölstrom und eine Bodenasphaltphase zu erhalten;
b. der deasphaltierte und demetallisierte Ölstrom in der Anwesenheit von Dampf thermisch gecrackt wird, um

einen gemischten Produktstrom zu erzeugen;
 c. der thermisch gecrackte, gemischte Produktstrom getrennt wird;
 d. Olefine und Aromaten von dem getrennten, gemischten Produktstrom rückgewonnen werden; und
 e. Pyrolyseschweröl von dem getrennten, gemischten Produktstrom rückgewonnen wird.

2. Integrierter Prozess nach Anspruch 1, wobei Schritt (c) umfasst, dass:

der thermisch gecrackte, gemischte Produktstrom mit mehreren Kompressionsstufen komprimiert wird;
 der komprimierte, thermisch gecrackte, gemischte Produktstrom einer Kaustikbehandlung unterzogen wird, um
 einen thermisch gecrackten, gemischten Produktstrom mit einem reduzierten Gehalt an Wasserstoffsulfid und
 Kohlendioxid zu erzeugen;
 der thermisch gecrackte, gemischte Produktstrom mit einem reduzierten Gehalt an Wasserstoffsulfid und Koh-
 lendioxid komprimiert wird;
 der komprimierte, thermisch gecrackte, gemischte Produktstrom mit einem reduzierten Gehalt an Wasserstoff-
 sulfid und Kohlendioxid dehydriert wird;
 Wasserstoff von dem dehydrierten, komprimierten, thermisch gecrackten, gemischten Produktstrom mit einem
 reduzierten Gehalt an Wasserstoffsulfid und Kohlendioxid rückgewonnen wird; und
 Olefine und Aromaten wie bei Schritt (d) und Pyrolyseschweröl wie bei Schritt (e) von dem Rest des dehydrierten,
 komprimierten, thermisch gecrackten, gemischten Produktstromes mit einem reduzierten Gehalt von Wasser-
 stoffsulfid und Kohlendioxid erhalten werden.

3. Integrierter Prozess nach Anspruch 2, ferner mit einem separaten Rückgewinnen von Methan von dem dehydrierten,
 komprimierten, thermisch gecrackten, gemischten Produktstrom mit einem reduzierten Gehalt an Wasserstoffsulfid
 und Kohlendioxid zur Verwendung als Brennstoff für Brenner und/oder Heizer in dem thermischen Crackschritt.

4. Integrierter Prozess nach Anspruch 1, wobei der Schritt zum thermischen Cracken umfasst, dass der deasphalтиerte
 und demetallisierte Ölstrom in einem Konvektionsabschnitt einer Dampfpyrolysezone erwärmt wird, der erwärmte
 deasphalтиerte und demetallisierte Ölstrom in eine Dampffracтion und eine Flüssigkeitsfracтion getrennt wird, die
 Dampffracтion in einem Pyrolyseabschnitt einer Dampfpyrolysezone geführt wird und die Flüssigkeitsfracтion aus-
 getragen wird.

5. Integrierter Prozess nach Anspruch 4, wobei die ausgetragene Flüssigkeitsfracтion mit Pyrolyseschweröl, das bei
 Schritt (e) rückgewonnen wird, gemischt wird.

6. Integrierter Prozess nach Anspruch 4, wobei das Trennen des erwärmten deasphalтиerten und demetallisierten
 Ölstroms in eine Dampffracтion und eine Flüssigkeitsfracтion mit einer Dampf-Flüssigkeits-Trennvorrichtung auf
 Grundlage physikalischer und mechanischer Trennung erfolgt.

7. Integrierter Prozess nach Anspruch 6, wobei die Dampf-Flüssigkeits-Trennvorrichtung umfasst:

ein Vorrotationselement mit einem Eintrittsabschnitt und einem Übergangsabschnitt, wobei der Eintrittsabschnitt
 einen Einlass zum Empfangen des strömenden Fluidgemisches sowie eine gekrümmte Leitung aufweist,
 einen gesteuerten Zyklonabschnitt, mit:

einem Einlass, der an das Vorrotationselement durch Konvergenz der gekrümmten Leitung und des Zy-
 klonabschnitts angrenzt,
 einen Steigleitungsabschnitt an einem oberen Ende des Zykloelementes, durch den Dämpfe gelangen;

und

einen Flüssigkeitssammler/-absetzabschnitt, durch den die Flüssigkeit gelangt.

8. Integrierter Prozess nach Anspruch 1, wobei Schritt (a) umfasst, dass
 der Rohölvorrat mit einem Aufbauölsemittel und optional frischem Lösemittel gemischt wird;
 das Gemisch an eine primäre Absetzeinrichtung übertragen wird, in der eine primäre deasphalтиerte und demetal-
 lisierte Ölphase und eine primäre Asphaltphase gebildet werden;
 die primäre deasphalтиerte und demetallisierte Ölphase zu einer sekundären Absetzeinrichtung übertragen wird, in
 der eine sekundäre deasphalтиerte und demetallisierte Ölphase und eine sekundäre Asphaltphase gebildet werden;
 die sekundäre Asphaltphase an die primäre Absetzeinrichtung rückgeführt wird, um zusätzliches deasphalтиertes

und demetallisiertes Öl rückzugewinnen;

die sekundäre deasphaltierte und demetallisierte Ölphase an eine Trennzone für deasphaltiertes und demetallisiertes Öl gefördert wird, um einen Rückfuhrlösemittelstrom und einen im wesentlichen lösemittelfreien deasphaltierten und demetallisierten Ölstrom zu erhalten; die primäre Asphaltphase an ein Trenngefäß zur Flashtrennung eines zusätzlichen Rückfuhrlösemittelstromes und einer Bodenasphaltphase gefördert wird, wobei der im Wesentlichen lösemittelfreie deasphaltierte und demetallisierte Ölstrom die Zufuhr zu der Dampfpyrolysezone darstellt.

9. Integrierter Prozess nach Anspruch 8, wobei die Bodenasphaltphase mit Pyrolyseschweröl gemischt wird, das bei Schritt (e) rückgewonnen wird.

Revendications

1. Procédé intégré de désasphaltage au solvant et de pyrolyse à la vapeur pour le traitement direct d'un pétrole brut pour produire des produits pétrochimiques oléfiniques et aromatiques, le procédé comprenant :

- a. le chargement du pétrole brut dans une zone de désasphaltage au solvant avec une quantité efficace de solvant pour produire un courant d'huile désasphaltée et démétalesée et une phase d'asphalte inférieure ;
- b. le craquage thermiquement du courant d'huile désasphaltée et démétalesée en présence de vapeur pour produire un courant de produit mélangé ;
- c. la séparation du courant de produit mélangé craqué thermiquement ;
- d. la récupération des oléfines et des composés aromatiques du courant de produit mélangé séparé ; et
- e. la récupération du mazout de pyrolyse du courant de produit mélangé séparé.

2. Procédé intégré selon la revendication 1, où l'étape (c) comprend
- la compression du courant de produit mélangé craqué thermiquement avec plusieurs étages de compression ;
 - la soumission du courant de produit mélangé craqué thermiquement comprimé à un traitement caustique pour produire un courant de produit mélangé craqué thermiquement avec une teneur réduite en sulfure d'hydrogène et en dioxyde de carbone ;
 - la compression du courant de produit mélangé craqué thermiquement avec une teneur réduite en sulfure d'hydrogène et en dioxyde de carbone ;
 - la déshydratation du courant de produit mélangé craqué thermiquement comprimé avec une teneur réduite en sulfure d'hydrogène et en dioxyde de carbone ;
 - la récupération de l'hydrogène du courant de produit mélangé craqué thermiquement comprimé avec une teneur réduite en sulfure d'hydrogène et en dioxyde de carbone ; et
 - l'obtention des oléfines et des composés aromatiques comme à l'étape (d) et le mazout de pyrolyse comme à l'étape (e) à partir du reste du courant de produit mélangé craqué thermiquement comprimé déshydraté avec une teneur réduite en sulfure d'hydrogène et en dioxyde de carbone.

3. Procédé intégré selon la revendication 2, comprenant en outre la récupération séparée de méthane à partir du courant de produit mélangé craqué thermiquement comprimé déshydraté avec une teneur réduite en sulfure d'hydrogène et en dioxyde de carbone pour une utilisation comme combustible pour des brûleurs et/ou des chauffages à l'étape de craquage thermique.

4. Procédé intégré selon la revendication 1, où l'étape de craquage thermique comprend le chauffage du courant d'huile désasphaltée et démétalesée dans une section de convection d'une zone de pyrolyse à la vapeur, la séparation du courant d'huile désasphaltée et démétalesée chauffée en une fraction vapeur et une fraction liquide, en faisant passer la fraction vapeur à une section de pyrolyse d'une zone de pyrolyse à la vapeur et le déchargement de la fraction liquide.

5. Procédé intégré selon la revendication 4 où la fraction liquide déchargée est mélangée avec du mazout de pyrolyse récupéré à l'étape (e).

6. Procédé intégré selon la revendication 4, où la séparation du courant d'huile désasphaltée et démétalesée chauffée en une fraction vapeur et une fraction liquide se fait avec un dispositif de séparation vapeur-liquide basé sur une séparation physique et mécanique.

7. Procédé intégré selon la revendication 6 où le dispositif de séparation vapeur-liquide comprend un élément de pré-rotation ayant une partie d'entrée et une partie de transition, la partie d'entrée ayant une entrée pour recevoir le mélange fluide en circulation et un conduit curviligne, une section cyclonique contrôlée ayant une entrée adjacente à l'élément de pré-rotation par la convergence du conduit curviligne et de la section cyclonique, une section de colonne montante au niveau d'une extrémité supérieure de l'organe cyclonique à travers laquelle des vapeurs passent ; et un collecteur de liquide/une section de sédimentation à travers lequel/laquelle le liquide passe.
8. Procédé intégré selon la revendication 1, où l'étape (a) comprend le mélange de la charge d'alimentation du pétrole brut avec un solvant d'appoint et un solvant éventuellement frais ; le transfert du mélange à un décanteur primaire dans lequel une phase d'huile primaire désasphaltée et démétalesée et une phase d'asphalte primaire sont formées ; le transfert de la phase d'huile primaire désasphaltée et démétalesée à un décanteur secondaire dans lequel une phase d'huile secondaire désasphaltée et démétalesée et une phase d'asphalte secondaire sont formées ; le recyclage de la phase d'asphalte secondaire au décanteur primaire pour récupérer de l'huile désasphaltée et démétalesée supplémentaire ; le transport de la phase d'huile secondaire désasphaltée et démétalesée dans une zone de séparation d'huile désasphaltée et démétalesée pour obtenir un courant de solvant de recyclage et un courant d'huile désasphaltée et démétalesée sensiblement sans solvant ; le transport de la phase d'asphalte primaire est transporté vers une cuve de séparation pour une séparation flash d'un courant de solvant de recyclage supplémentaire et d'une phase d'asphalte inférieure, où le courant d'huile désasphaltée et démétalesée sensiblement sans solvant est l'alimentation de la zone de pyrolyse à la vapeur.
9. Procédé intégré selon la revendication 8, où la phase d'asphalte inférieure est mélangée avec du mazout de pyrolyse récupéré à l'étape (e).

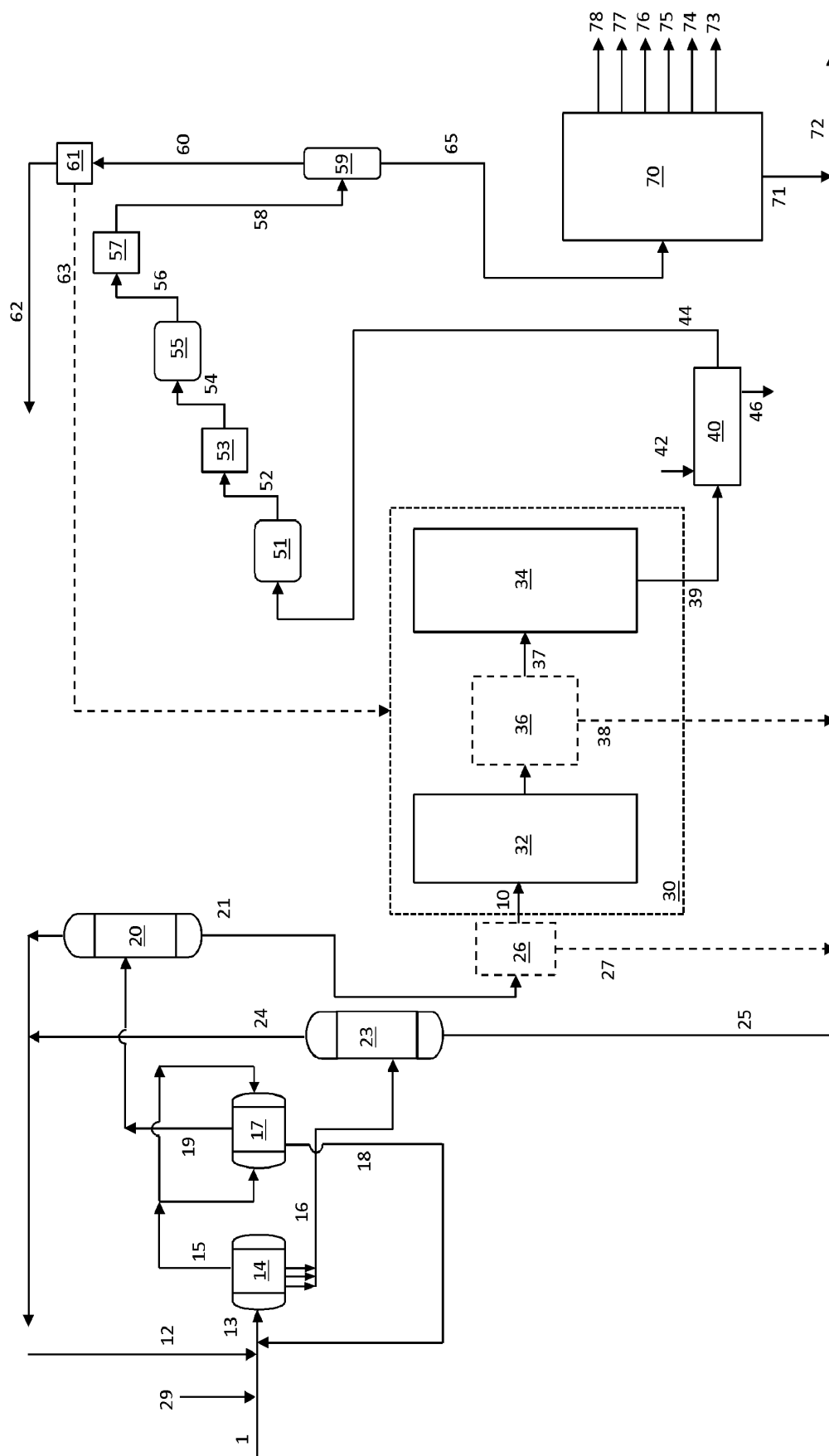
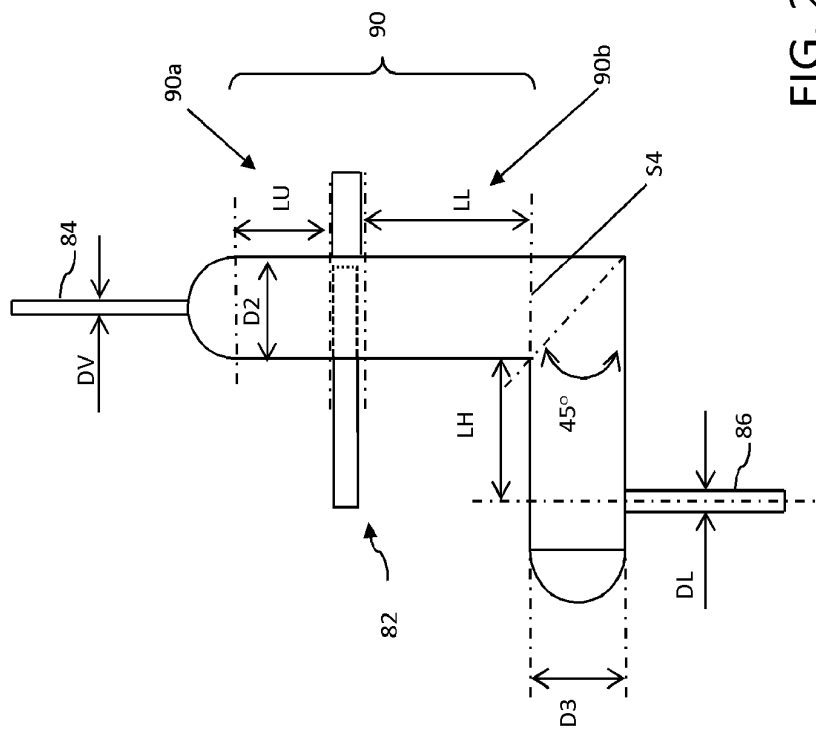
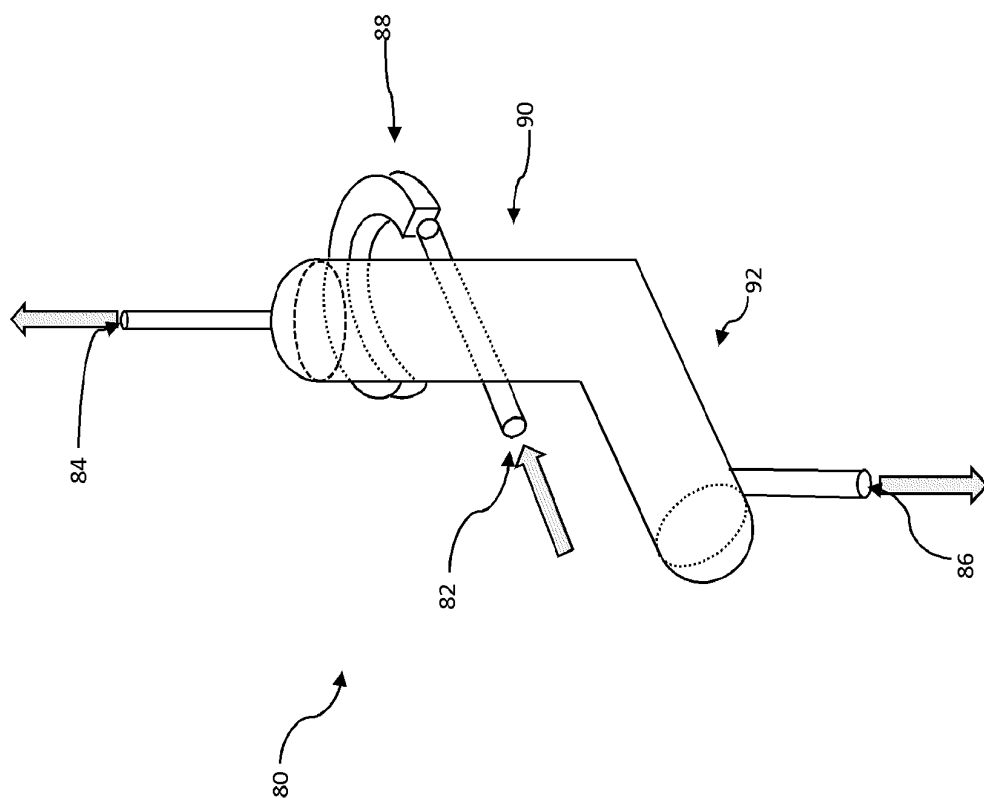
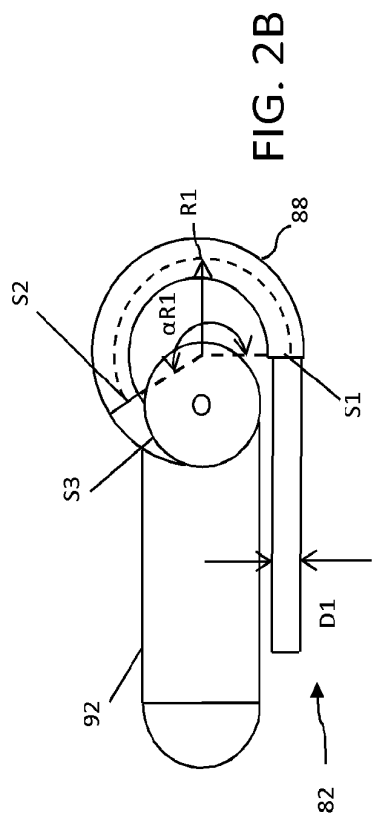


FIG. 1



REFERENCES CITED IN THE DESCRIPTION

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