(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
11 June 2015 (11.06.2015)

WIPO | PCT

(10) International Publication Number
WO 2015/084779 A1

(51) International Patent Classification:
C10G 55/06 (2006.01) *C10G 21/00* (2006.01)
C10G 11/18 (2006.01)

(21) International Application Number:
PCT/US2014/068034

(22) International Filing Date:
2 December 2014 (02.12.2014)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/910,676 2 December 2013 (02.12.2013) US

(71) Applicants: SAUDI ARABIAN OIL COMPANY [SA/SA]; Box 5000, Dhahran, 31311 (SA). **ARAMCO SERVICES COMPANY** [US/US]; 9009 West Loop South, Houston, TX 77096 (US).

(72) Inventors; and
(71) Applicants *(for US only)*: **SHAFI, Raheel** [GB/BH]; Nexant Ltd., Level 22, West Tower, Bahrain Financial Harbour, Manama (BH). **BOURANE, Abdennour** [FR/SA]; P.O. Box 1634, Saudi Aramco, Ras Tanura (SA). **AL-GHRAMI, Musaed, Salem** [SA/SA]; P.O. Box 10587, Saudi Aramco, Dhahran, 31311 (SA). **ABUDAWOUD, Raed** [SA/SA]; P.O. Box 6970, Saudi Aramco, Dhahran, 31311 (SA).

(74) Agent: CRISPINO, Ralph, J.; Abelman, Frayne & Schwab, 666 Third Avenue, New York, NY 10017-5621 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report (Art. 21(3))*

(54) Title: INTEGRATED SOLVENT-DEASPHALTING AND FLUID CATALYTIC CRACKING PROCESS FOR LIGHT OLEFIN PRODUCTION

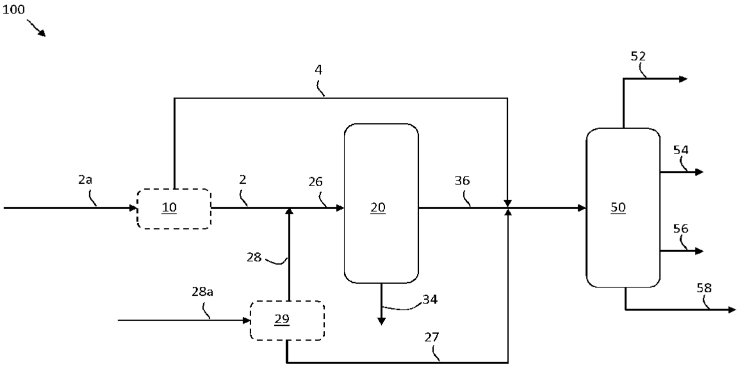

FIG. 1

(57) Abstract: The process described herein broadly comprehends an integrated process that permits the use of straight run residual fractions as a feedstock to produce lighter olefins including propylene. A blend of natural gas condensate and/or naphtha, and heavy oil residue(s), is catalytically cracked to produce a light olefin-rich product stream. In particular, the light natural gas condensate and/or naphtha stream is used as both solvent in a solvent-deasphalting unit and a portion for the feedstock to a fluidized catalytic cracking process. In addition, blending a heavy boiling hydrocarbon stream with a light natural gas condensate or naphtha stream enables efficient cracking in fluidized catalytic cracking process processes while sustaining the heat balance within the cracking unit.

INTEGRATED SOLVENT-DEASPHALTING AND FLUID CATALYTIC CRACKING PROCESS FOR LIGHT OLEFIN PRODUCTION

RELATED APPLICATIONS

[01] The present application claims the benefit of U.S. Provisional Patent Application No. 61/910,676 filed on 02 December 2013, the disclosure of which is incorporated herein by reference in its entirety.

BACKGROUND OF THE INVENTION

Field of the Invention

[02] The present invention relates to an integrated solvent deasphalting and high-severity catalytic cracking process for the production of light olefins, particularly propylene.

Description of Related Art

[03] Light olefins are basic intermediates for a large number of processes in the petrochemical industry. They are typically obtained through the thermal cracking (or steam pyrolysis) of petroleum gases and distillates such as naphtha, kerosene or in some instances gas oil. However, thermal cracking typically yields higher rates of ethylene than it does propylene, which has significant market demand.

[04] In particular, there are often shortages of propylene which result in uncertainties in the supply of feedstocks, escalating raw material costs and similar commercial detriments. Additionally, due to uncertainties in the valuations of different hydrocarbon fractions, alternative feedstocks for propylene production are desirable.

[05] Fluidized catalytic cracking is a well-known process that can be tailored to provide relatively higher selectivity of propylene over ethylene, particularly as compared to steam pyrolysis. Common feeds for fluidized catalytic cracking processes include vacuum gas oil, hydrotreated bottoms, hydrocracked bottoms and crude oil residuum. However, these feeds do not typically result in high olefin product yields and require costly pretreatment steps to increase the hydrogen content.

[06] Therefore, a need remains for improved processes and systems for high olefin product yields while minimizing the need to use valuable hydrocarbon fractions from within a refinery.

SUMMARY OF THE INVENTION

[07] It is an objective of the present invention to provide a process in which alternative feedstocks are cracked using fluidized catalytic cracking to increase the proportion of lighter olefins, in particular propylene.

[08] The process described herein broadly comprehends an integrated process that permits the use of straight run residual fractions as a feedstock to produce lighter olefins including propylene.

[09] For the process described herein a new type of feedstream is provided to the integrated system and process in order to maximize light olefins production. A blend of natural gas condensate and/or naphtha, and heavy oil residue(s), is catalytically cracked to produce a light olefin-rich product stream. In particular, the light natural gas condensate and/or naphtha stream is used as both solvent in a solvent-deasphalting unit and a portion for the feedstock to a fluidized catalytic cracking process. In addition, blending a heavy boiling hydrocarbon stream with a light natural gas condensate or naphtha stream enables efficient cracking in fluidized catalytic cracking process processes while sustaining the heat balance within the cracking unit.

[10] Before being catalytically cracked to a stream rich in light olefins, the light crude oil fractions, such as naphtha and/or natural gas condensates, are used as the solvent in a solvent deasphalting unit, where the metallic and asphaltenic compounds, that could poison the fluidized catalytic cracking catalysts, are removed from the heavy residual oil fraction (such as atmospheric or vacuum distillation residue). This allows obtaining a mixture of the light hydrocarbon fraction and deasphalted heavy feed that has reduced level amounts of metals, sulfur, nitrogen, ash, and Conradson carbon.

[11] The light streams that are blended in the integrated generally comprise hydrocarbons with carbon numbers in the range of 5-7, where the deasphalted oil is solubilized in the solvent. The insoluble pitch will precipitate out of the mixed solution and is separated from the mixture of solvent and deasphalted/demetalized oil in one or more extractors.

[12] Still other aspects, embodiments, and advantages of these exemplary aspects and embodiments, 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 aspects and embodiments. The accompanying drawings are included to provide illustration and a further understanding of the various aspects and embodiments, and are incorporated in and constitute a part of this specification. The drawings, together with the remainder of the specification, serve to explain principles and operations of the described and claimed aspects and embodiments.

BRIEF DESCRIPTION OF THE DRAWINGS

[13] The present process will be described in further detail below and with reference to the attached drawings in which the same or similar reference number is used to refer to the same and similar elements, and in which:

[14] FIG. 1 is a schematic flow diagram of an embodiment of apparatus for fluidized catalytic cracking of a natural gas condensate and/or naptha blended with a heavy oil residue(s) feedstream suitable for production of light olefins including propylene;

[15] FIG. 2 is a simplified schematic illustration of a solvent deasphalting/demetalizing system;

[16] FIG. 3 is a simplified schematic illustration of a downflow fluidized catalytic cracking reactor system; and

[17] FIG. 4 is a simplified schematic illustration of a riser fluidized catalytic cracking reactor system.

DETAILED DESCRIPTION OF THE INVENTION

[18] Due to increasing demand for propylene, new feedstock sources are desired for its production. The processes and systems described herein utilize feedstock sources for fluidized catalytic cracking including natural gas condensates and petroleum naphthas, along with residual fractions, directly from atmospheric or vacuum distillation bottoms, in an integrated process including solvent deasphalting and fluidized catalytic cracking. The integrated process maximizes the yield of light olefins, including propylene.

[19] FIG. 1 is a schematic flow diagram including integrated solvent deasphalting and fluidized catalytic cracking processes. The system generally includes a solvent deasphalting/demetalizing zone **20** and a fluidized catalytic cracking reaction and separation zone **50**.

[20] In certain embodiments, an initial feedstock **2** is charged to the solvent deasphalting zone **20** along with a solvent feedstock **28** in which it is subjected to conventional solvent deasphalting processes, and an asphalt phase is discharged via outlet **34**. The deasphalted/demetalized oil, in combination with the solvent feedstock that is used for deasphalting operations in place of conventional solvent that is typically recycled from the system, is passed via a stream **36** to the fluidized catalytic cracking reaction and separation zone **50**. Fluidized catalytic cracking reactions occur under conditions that maximize formation of light olefins, including propylene, and products including light gases **52**, olefins **54**, gasoline **56** and cycle oil **58** are recovered from a separation zone.

[21] In certain embodiments, an optional splitter **10** is provided which receives all or a portion of an initial feedstock **2a** and is in fluid communication with the fluidized catalytic

cracking reaction and separation zone **50** to pass a light fraction **4** thereto and the solvent deasphalting zone **20** to pass a heavy fraction **2** thereto. In these embodiments the light fraction **4** is recombined with stream **36** containing deasphalted/demetalized oil and solvent feedstock, and is charged to the fluidized catalytic cracking reaction and separation zone **50**.

[22] In certain embodiments, an optional splitter **29** is provided which receives all or a portion of the initial solvent feedstock **28a** and is in fluid communication with the fluidized catalytic cracking reaction and separation zone **50** to pass a heavy fraction **27** of the solvent feedstock thereto and the solvent deasphalting zone **20** to pass a light fraction **28** thereto. In these embodiments the light fraction **28** serves as the solvent in the solvent deasphalting/demetalizing zone **20** and the heavy fraction **27** is combined with stream **36** containing deasphalted/demetalized oil and solvent feedstock, and is charged to the fluidized catalytic cracking reaction and separation zone **50**.

[23] In additional embodiments (not shown), a relatively small portion of stream **36**, particularly all or a portion of C5 and lower components, can be recycled to solvent deasphalting/demetalizing zone **20** or flashed off, since these compounds will not be completely cracked under the herein FCC conditions. For instance, these C5 and lower components derived from Khuff condensate can be recycled or flashed.

[24] Unit operations associated with the fluidized catalytic cracking reaction and separation zone **50** and solvent deasphalting zone **20** are described below. In the interest of clarity, the numerous valves, temperature sensors, electronic process controllers and the like that are customarily employed, and that are well known to those of ordinary skill in the art of solvent deasphalting/demetalizing and fluidized catalyst cracking, are not included in the attached schematic illustration. Accessory systems that are utilized in conventional fluidized catalyst cracking systems such as, for example, air supply, catalyst hoppers, torch oil supply, flue gas handling and heat recovery, fresh and spent catalyst hoppers for storage of make-up

and used/equilibrium catalyst that can be added to, or removed from the regenerator, are not shown.

[25] According to the present process and system, the solvent in the solvent deasphalting/demetalizing operation is not separated from the deasphalted/demetalized oil, contrary to conventional solvent deasphalting/demetalizing operations.

[26] Solvent deasphalting/demetalizing is generally carried-out in liquid phase and therefore the temperature and pressure are set accordingly at or below the critical temperature and pressure of the solvent. In a typical two-stage solvent deasphalting/demetalizing process, the temperature is lower in the first stage than that of the second stage to separate the bulk of the asphaltenes. The second stage temperature is set to control the deasphalted/demetalized oil quality and quantity. The temperature has a large impact on the quality and quantity of deasphalted/demetalized oil. An extraction temperature increase will result in a decrease in deasphalted/demetalized oil yield, in turn the deasphalted/demetalized oil will be lighter, less viscous, and contain less metals, asphaltenes, sulfur, and nitrogen. A temperature decrease will have the opposite impact. In general, the deasphalted/demetalized yield decreases with higher quality product by raising the extraction system temperature, and the deasphalted/demetalized yield increases with lower quality product by lowering extraction system temperature.

[27] In conventional solvent deasphalting/demetalizing operations, composition of the solvent is an important process variable. The solubility properties of the solvent increases with increasing critical temperature, $C3<iC4<nC4<iC5$. An increase in critical temperature of the solvent increases the deasphalted/demetalized oil yield. However, it should be noted that solvents possessing higher critical temperatures have lower selectivity resulting in lower deasphalted/demetalized oil quality. According to certain embodiments of the process herein, in which naphtha or natural gas condensates are used as a solvent in the solvent deasphalting/demetalizing operation, all or a portion of the heavy-end components of the

naphtha or natural gas condensates are removed by fractionation and the lighter portion of the stream is used in the solvent deasphalting/demetalizing process.

[28] The ratio of the light fraction (solvent feedstock) to the heavy fraction (oil feedstock) entering the deasphalting/demetailzing unit impacts selectivity and to a lesser degree yield of deasphalted/demetalized oil. The major effect of light to heavy stream ratio is that a higher ratio results in a higher quality of the deasphalted/demetalized oil for a given fixed deasphalted/demetalized yield. A high solvent (light fraction) to heavy fraction ratio is preferred in certain embodiments due to of enhanced selectivity. In the process and system herein, ratio of the light to the heavy fraction entering the deasphalting/demetailzing unit is determined as a function of the coke that will be produced during the cracking reaction within the fluidized catalytic cracking reaction, as described further herein. The solvent-to-oil ratio is in the range of about 5:1 to about 50:1, in certain embodiments in the range of about 5:1 to about 25:1, and in further embodiments in the range of about 5:1 to about 15:1. The ratio of the light to heavy fraction of the hydrocarbon mixture fed to the fluidized catalytic cracking process is manipulated not only to ensure generation of sufficient coke in the cracking reactions so as to maintain a heat balance in the fluidized catalytic cracking unit, but also to facilitate optimal conversion to obtain high light olefins yield.

[29] The solvent deasphalting unit is operated at a pressure that is sufficiently high to maintain the solvent in the liquid phase within the extraction system. The pressure is typically considered as a variable and is typically not altered unless the solvent composition varies.

[30] FIG. 2 is a simplified schematic illustration of a solvent deasphalting/demetalizing system. Exemplary unit operations within solvent deasphalting zone **20** of the integrated system described with respect to FIG. 1 are shown. While the system and process is shown with primary and secondary extraction zones, it should be appreciated that one extraction zone can be used, or alternatively more than two extraction zones can be used.

[31] A solvent deasphalting zone **120** typically includes a primary extraction zone **122** and a secondary extraction zone **124**. Primary extraction zone **122** includes an inlet for receiving a combined stream **126** including the hydrocarbon feedstock **102** (or a heavy portion thereof in embodiments in which the optional splitter **110** is used) and a solvent feedstock **128**. Primary extraction zone **122** also includes an outlet for discharging a primary deasphalted/demetalized oil phase **132** and one or more outlets for discharging a primary asphalt phase **133**. Secondary extraction zone **122** typically includes an inlet for receiving the primary deasphalted/demetalized oil phase **132**, an outlet for discharging a secondary deasphalted/demetalized oil phase **136** and an outlet for discharging a secondary asphalt phase **137**. The combined primary asphalt phase **133** and secondary asphalt phase **137**, stream **134**, is passed to an asphalt pool **144**.

[32] According to the process herein, the solvent feedstock **128** is selected so as to be suitable not only as a solvent for facilitating precipitation of the asphalt phase **134** of the feedstock **102**, but also to serve as a reactant in the downstream fluidized catalytic cracking process to yield fluidized catalytic cracking products olefins, gasoline and cycle oil, with a maximized propylene yield. Therefore the solvent deasphalting zone **120** does not require separate solvent recovery/recycle steps or unit operations since the solvent component is part of the combined stream **136** that is the feed to the fluidized catalytic cracking reaction.

[33] In general, during fluidized catalytic cracking processes, petroleum derived hydrocarbons are catalytically cracked with an acidic catalyst maintained in a fluidized state, which is regenerated on a continuous basis. The main product from such processes has conventionally been gasoline. Other products are also produced in smaller quantities via fluidized catalytic cracking such as liquid petroleum gas and cycle oil. Coke deposited on the catalyst is burned off at high temperatures and in the presence of air prior to recycling regenerated catalyst back to the reaction zone. As discussed above, a shift in market demands has led to use of fluidized catalytic cracking for production of light olefins,

including propylene, as a primary product. These operations have significant economic advantages, particularly with respect to oil refineries that are highly integrated with petrochemical production facilities.

[34] According to the processes and systems herein, a high-severity fluid catalytic cracking process is used to facilitate conversion of the feed into a product rich in light olefins. For instance, a PetroFCC process (disclosed by UOP, a Honeywell International Inc. company) can be suitable for the present processes and systems. In general, suitable high-severity fluid catalytic cracking processes result in minimization of olefin consuming reactions thereby maximizing the yield of light olefin products such as propylene.

[35] In certain embodiments, a fluidized catalytic cracking unit configured with a downflow reactor is provided that operates under conditions that promote formation of olefins, particularly propylene, and that minimize olefin-consuming reactions including hydrogen-transfer reactions. FIG. 3 is a simplified schematic illustration of a downflow fluidized catalytic cracking unit. Exemplary unit operations within fluidized catalytic cracking zone **50** of the integrated system described with respect to FIG. 1 are shown. A fluidized catalytic cracking unit **250** includes a reactor/separator **260** having a reaction zone **262** and a separation zone **264**. Fluidized catalytic cracking unit **250** also includes a regeneration zone **266** for regenerating spent catalyst. In particular, a charge **236** (which is the combined stream of deasphalted/demetalized and solvent feed, and in certain embodiments recombined with light ends of the feed and/or heavy ends of the solvent as described above) is introduced to the reaction zone, in certain embodiments accompanied by steam or other suitable gas for atomization of the feed (not shown). An effective quantity of heated fresh or hot regenerated solid cracking catalyst particles from regeneration zone **266** is conveyed to the top of reaction zone **262** also transferred, e.g., through a downwardly directed conduit or pipe **268**, commonly referred to as a transfer line or standpipe, to a withdrawal well or hopper (not shown) at the top of reaction zone **262**. Hot catalyst flow is

typically allowed to stabilize in order to be uniformly directed into the mix zone or feed injection portion of reaction zone **262**. The charge **236** is injected into a mixing zone through feed injection nozzles typically situated proximate to the point of introduction of the regenerated catalyst into reaction zone **262**. These multiple injection nozzles result in the catalyst and oil mixing thoroughly and uniformly. Once the charge contacts the hot catalyst, cracking reactions occur.

[36] The reaction vapor of hydrocarbon cracked products, unreacted feed and catalyst mixture quickly flows through the remainder of reaction zone **262** and into the rapid separation zone **264** at the bottom portion of reactor/separator **260**. Cracked and uncracked hydrocarbons are directed through a conduit or pipe **270** to a conventional product recovery section known in the art to yield fluidized catalytic cracking products olefins, gasoline and cycle oil, with a maximized propylene yield. If necessary for temperature control, a quench injection can be provided near the bottom of reaction zone **262** immediately before the separation zone **264**. This quench injection quickly reduces or stops the cracking reactions and can be utilized for controlling cracking severity.

[37] The reaction temperature, i.e., the outlet temperature of the downflow reactor, can be controlled by opening and closing a catalyst slide valve (not shown) that controls the flow of regenerated catalyst from regeneration zone **266** into the top of reaction zone **262**. The heat required for the endothermic cracking reaction is supplied by the regenerated catalyst. By changing the flow rate of the hot regenerated catalyst, the operating severity or cracking conditions can be controlled to produce the desired yields of light olefinic hydrocarbons. A stripper **272** is also provided for separating oil from the catalyst, which is transferred to regeneration zone **266**. The catalyst from separation zone **264** flows to the lower section of the stripper **272** that includes a catalyst stripping section into which a suitable stripping gas, such as steam, is introduced through streamline **274**. The stripping section is typically provided with several baffles or structured packing (not shown) over which the downwardly

flowing catalyst **280** passes counter- currently to the flowing stripping gas. The upwardly flowing stripping gas, which is typically steam, is used to "strip" or remove any additional hydrocarbons that remain in the catalyst pores or between catalyst particles. The stripped or spent catalyst is transported by lift forces from the combustion air stream **276** through a lift riser of the regeneration zone **264**. This spent catalyst, which can also be contacted with additional combustion air, undergoes controlled combustion of any accumulated coke. Flue gases are removed from the regenerator via conduit **278.** In the regenerator, the heat produced from the combustion of the by-product coke is transferred to the catalyst raising the temperature required to provide heat for the endothermic cracking reaction in the reaction zone **262**. According to the process herein, since the light solvent feedstock is combined with the heavy feedstock as the feed **236**, the solvent to oil ratio in the initial solvent deasphalting/demetalizing process is selected so as to provide sufficient coking of the catalyst to provide the heat balance during regeneration.

[38] In one embodiment, a suitable fluidized catalytic cracking unit **250** that can be employed in the integrated solvent deasphalting and high-severity catalytic cracking system and process described herein can be similar to those described in US Patent Number 6,656,346, and US Patent Publication Number 2002/0195373, both of which are incorporated herein by reference. Important properties of downflow reactors include introduction of feed at the top of the reactor with downward flow, shorter residence time as compared to riser reactors, and high catalyst to oil ratio, e.g., in the range of about 20:1 to about 30:1.

[39] In general, the operating conditions for the reactor of a suitable downflow FCC unit include:

reaction temperature of about 500°C to about 650°C, in certain embodiments about 550°C to about 630°C, and in further embodiments about 570°C to about 610°C;

reaction pressure of about 1 Kg/cm^2 to about 5 Kg/cm^2, in certain embodiments of about 1 Kg/cm^2 to about 3 Kg/cm^2, in further embodiments of about 1 Kg/cm^2 to about 2 Kg/cm^2;

contact time (in the reactor) of about 0.1 seconds to about 10 seconds, in certain embodiments of about 0.1 seconds to about 5 seconds, in further embodiments of about 0.2 seconds to about 0.8 seconds; and

a catalyst to feed ratio of about 2:1 to about 40:1, in certain embodiments of about 2:1 to about 30:1, in further embodiments of about 2:1 to about 20:1.

[40] In certain embodiments, a fluidized catalytic cracking unit configured with a riser reactor is provided that operates under conditions that promote formation of olefins, particularly propylene, and that minimize olefin-consuming reactions including hydrogen-transfer reactions. FIG. 4 is a simplified schematic illustration of a riser fluidized catalytic cracking unit. Exemplary unit operations within fluidized catalytic cracking zone **50** of the integrated system described with respect to FIG. 1 are shown. A fluidized catalytic cracking unit **350** which includes a riser reactor and can be used in the herein integrated solvent deasphalting and high-severity catalytic cracking system and process. Fluidized catalytic cracking unit **350** includes a reactor/separator **360** having a riser portion **361**, a reaction zone **363** and a separation zone **365**. Fluidized catalytic cracking unit **350** also includes a regeneration vessel **367** for regenerating spent catalyst. A charge **336** (which is the combined stream of deasphalted/demetalized and solvent feed, and in certain embodiments recombined with light ends of the feed and/or heavy ends of the solvent as described above) is introduced to the reaction zone, in certain embodiments accompanied by steam or other suitable gas for atomization of the feed (not shown). The charge **336** is admixed and intimately contacted with an effective quantity of heated fresh or regenerated solid cracking catalyst particles which are conveyed via a conduit **369** from regeneration vessel **367**. The feed mixture and the cracking catalyst are contacted under conditions to form a suspension that is introduced into the riser **361**. In a continuous process, the mixture of cracking catalyst and hydrocarbon feedstock proceed upward through the riser **361** into reaction zone **363**. In riser **361** and reaction zone **363**, the hot cracking catalyst particles catalytically crack relatively large hydrocarbon molecules by carbon-carbon bond cleavage.

[41] During the reaction, as is conventional in fluidized catalytic cracking operations, the cracking catalysts become coked and hence access to the active catalytic sites is limited or nonexistent. Reaction products are separated from the coked catalyst using any suitable configuration known in a fluidized catalytic cracking units, generally referred to as the separation zone **365** in a fluidized catalytic cracking unit **350**, for instance, located at the top of the reactor **360** above the reaction zone **363**. The separation zone can include any suitable apparatus known to those of ordinary skill in the art such as, for example, cyclones. The reaction product is withdrawn through conduit **371**. Catalyst particles containing coke deposits from fluid cracking of the hydrocarbon feedstock pass through a conduit **373** to regeneration zone **367**. According to the process herein, since the light solvent feedstock is combined with the heavy feedstock as the feed **336**, the solvent to oil ratio in the initial solvent deasphalting/demetalizing process is selected so as to provide sufficient coking of the catalyst to provide the heat balance during regeneration.

[42] In regeneration zone **367**, the coked catalyst comes into contact with a stream of oxygen-containing gas, e.g., pure oxygen or air, which enters regeneration zone **367** via a conduit **375**. The regeneration zone **367** is operated in a configuration and under conditions that are known in typical a fluidized catalytic cracking operations. For instance, regeneration zone **367** can operate as a fluidized bed to produce regeneration off-gas comprising combustion products which is discharged through a conduit **377**. The hot regenerated catalyst is transferred from regeneration zone **367** through conduit **369** to the bottom portion of the riser **361** for admixture with the hydrocarbon feedstock and noted above.

[43] In one embodiment, a suitable a fluidized catalytic cracking unit **350** that can be employed in the integrated solvent deasphalting and high-severity catalytic cracking system

and process described herein can be similar to that described in US Patent Numbers 7,312,370, 6,538,169, and 5,326,465, which are incorporated herein by reference.

[44] In general, the operating conditions for the reactor of a suitable riser fluidized catalytic cracking unit include:

reaction temperature of about 500°C to about 650°C, in certain embodiments about 550°C to about 630°C, and in further embodiments about 570°C to about 610°C;

reaction pressure of about 1 Kg/cm^2 to about 5 Kg/cm^2, in certain embodiments of about 1 Kg/cm^2 to about 3 Kg/cm^2, in further embodiments of about 1 Kg/cm^2 to about 2 Kg/cm^2;

contact time (in the reactor) of about 0.7 seconds to about 10 seconds, in certain embodiments of about 1 second to about 5 seconds, in further embodiments of about 1 second to about 2 seconds ; and

a catalyst to feed ratio of about 2:1 to about 40:1, in certain embodiments of about 2:1 to about 25:1, in further embodiments of about 2:1 to about 15:1.

[45] The catalyst or catalyst systems that can be used in the process described herein are not limited. A catalyst that is suitable for the particular charge and the desired product is conveyed to the FCC reactor within the FCC reaction and separation zone. In certain embodiments, to promote formation of olefins and minimize olefin-consuming reactions, such as hydrogen-transfer reactions, an FCC catalyst mixture is used in the FCC reaction and separation zone, including an FCC base catalyst and an FCC catalyst additive.

[46] In particular, a matrix of a base cracking catalyst can include one or more clays such as kaolin, montmorilonite, halloysite and bentonite, and/or one or more inorganic porous oxides such as alumina, silica, boria, chromia, magnesia, zirconia, titania and silica-alumina. The base cracking catalyst preferably has a bulk density of 0.5 g/ml to 1.0 g/ml, an average particle diameter of 50 microns to 90 microns, a surface area of 50 m^2/g to 350 m^2/g and a pore volume of 0.05 ml/g to 0.5 ml/g.

[47] A suitable catalyst mixture contains, in addition to a base cracking catalyst, an additive containing a shape-selective zeolite. The shape selective zeolite referred to herein means a zeolite whose pore diameter is smaller than that of Y-type zeolite, so that hydrocarbons with only limited shape can enter the zeolite through its pores. Suitable shape-selective zeolite components include ZSM-5 zeolite, zeolite omega, SAPO-5 zeolite, SAPO-11 zeolite, SAPO34 zeolite, and pentasil-type aluminosilicates. The content of the shape-selective zeolite in the additive is generally in the range of 20 to 70 wt%, and preferably in the range of 30 to 60 wt%.

[48] The additive preferably has a bulk density of 0.5 g/ml to 1.0 g/ml, an average particle diameter of 50 microns to 90 microns, a surface area of 10 m^2/g to 200 m^2/g and a pore volume of 0.01 ml/g to 0.3 ml/g.

[49] A percentage of the base cracking catalyst in the catalyst mixture can be in the range of 60 to 95 wt% and a percentage of the additive in the catalyst mixture is in a range of 5 to 40 wt%. If the percentage of the base cracking catalyst is lower than 60 wt% or the percentage of additive is higher than 40 wt%, high light-fraction olefin yield cannot be obtained, because of low conversions of the feed oil. If the percentage of the base cracking catalyst is higher than 95 wt%, or the percentage of the additive is lower than 5 wt%, high light-fraction olefin yield cannot be obtained, while high conversion of the feed oil can be achieved.

[50] The initial heavy feedstock for use in above-described systems and processes can be a straight run residue obtained from atmospheric distillation and/or vacuum distillation. In general, the feedstock contains hydrocarbons having boiling point greater than about 380°C in the case of atmospheric residue, and greater than about 540°C in the case of vacuum residue. The source of the residues can be crude oil, synthetic crude oil, bitumen, oil sand, shell oil, coal liquids, or a combination including one of the foregoing sources.

[51] In a process using the system of FIG. 1, all or a portion of the light stream 28a (naphtha or natural gas condensate of carbon range starting at C5 or above) is first fed to an optional splitter 29 to remove a heavy portion 27 thereof, if required to optimize the solvent deasphalting/demetalizing operation. The light portion 28 is admixed with a heavy oil fraction 2, such as atmospheric or vacuum residue. The resulting mixture 26 is then transferred to the solvent deasphalting/demetalizing zone 20, for instance, which can be operated in a manner similar to what is reported in B.M. Yezhov, A.S. Aigenson, G.A. Berg, F.Kh. Malikov, Yu.S. Sabadash and G.A. Vorms, *Hydrocarbon Separation, including Engineering Developments*, 1971, 8th World Petroleum Congress, 221-227, which is incorporated herein by reference, in which a gasoline-type stream is used as the solvent to extract asphaltenes from a heavy hydrocarbon fraction. The asphaltenes 34 are rejected from the hydrocarbon mixture and the resultant mixture 36 is directly sent to the fluidized catalytic cracking zone 50. In embodiments in which the optional splitter is used to remove a heavy portion of the solvent feedstream prior to mixing with the heavy fraction 2, the heavy portion 27 is recombined with the feed passed to the fluidized catalytic cracking zone 50.

[52] Advantageously, the processes and systems described herein accommodate the high demand for light olefins with the use of alternative feedstocks including hydrocarbons in lighter boiling-ranges than those which are usually used as fluidized catalytic cracking feeds. These lighter feeds include natural gas condensates and petroleum naphthas.

[53] The problems that arise when lighter feedstocks are used in the fluidized catalytic cracking feeds process is the low coking on the catalyst. This lower amount of coke is not sufficient to provide the heat for catalytic regeneration in the fluidized catalytic cracking process. Therefore, an additional heat source would typically be required for the fluidized catalytic cracking process to operate properly. However, according to the process herein, blending an effective quantity of a very heavy fraction, such as atmospheric or vacuum residue, with the light fraction(s) can result in sufficient coke for catalyst regeneration.

[54] Using the lighter feeds as blends, however, does not counter the negative impacts that result from use of straight run residues (i.e., those directly from atmospheric an./or vacuum distillation) such as catalyst poisoning due to metal and asphaltenic content of the heavy oil fractions. In order to avoid poisoning the fluidized catalytic cracking catalyst these compounds must be removed from the heavy fraction, which leads to a better overall process performance and longer catalyst life. According to the process herein, these metals and asphaltenes are removed by a tightly integrated solvent deasphalting/demetalizing process, in which the solvent also serves as the feedstock blend to increase propylene yield.

[55] It is to be understood that the present processes contemplate use of the naphtha or natural gas condensate as a solvent and reactant. This is in contrast to known processes such as that disclosed in Bartilucci et al. US Patent 5,000,838 in which naphtha that may remain in a deasphalted oil does not serving as a reactant to produce light olefins. In that process, the boiling range of the cracking product is 100 – 400 °F (37.8 – 204.4 °C), whereas light olefins (ethylene and propylene) boil in the range of -155 to -54 °F (-103.9 to -47.8 °C) indicating that the fluidized catalytic cracking process described therein is operated at conditions through which light olefins cannot be produced and that any naphtha in the cracking feed does not react at all, since one would expect the boiling range of the product to be less than the feed if cracking reactions were to occur.

Example

[56] An atmospheric residue derived from atmospheric distillation of a crude oil was mixed with gas condensate at a volumetric condensate:residue ratio of 10:1 for partial deasphalting. The mixture was stirred at room temperature, them maintained for a few hours to settle, and filtered to separate the precipitated material. About 5wt% of the atmospheric residue was precipitated. The properties of the atmospheric residue, condensate and obtained deasphalted mixture are given in Table 1 below.

Table 1			
	Atmospheric Residue	Gas Condensate	Deasphalted Mixture
Gravity, Specific 60/60 °F	0.9651	0.7721	0.7796
Sulfur, Total Wt %	3.2	0.0521	0.0560
Vanadium, ppm	29	-	1.4
Microcarbon Residue, wt%	6.2	0.01	0.31
Nickel, ppm	9	-	<2

[57] Catalytic cracking of the deasphalted mixture was conducted using a micro activity testing (MAT) unit well known to a person of ordinary skill in the art at 600°C and a C/O ratio of ~4. The catalyst contains a mixture of Y zeolite and ZSM-5. The cracking of the gas condensate alone was also similarly performed and the products yields difference (relative) are shown in Table 2. As seen, more coke can be produced from the mixture feed while maintaining propylene yield.

Table 2	
Product Yields	Deasphalted Mixture Vs Gas condensate relative difference (%)
Dry gas	+3
LPG	-6
propylene	-6
gasoline	-1
LCO	+20
HCO	+17
Coke	+28

[58] The process 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 process for production of propylene comprising:

mixing a residual oil feedstream with a solvent in quantities and under conditions sufficient to precipitate at least a fraction of the asphaltenes, thereby producing a mixture of solvent and deasphalted residual oil, and precipitated asphaltenes, and;

subjecting the mixture of solvent and deasphalted residual oil to fluidized catalytic cracking reactions, wherein both the solvent and the deasphalted residual oil from the mixture of solvent and deasphalted residual oil serve as reactants in the fluidized catalytic cracking reaction.

2. The process as in claim 1 wherein the mixture of solvent and deasphalted residual oil is not subjected to solvent recovery prior to fluidized catalytic cracking reactions.

3. The process as in claim 1 wherein subjecting the mixture of solvent and deasphalted residual oil to fluidized catalytic cracking reactions occurs under high-severity fluid catalytic cracking conditions to facilitate conversion of reactants into a product rich in light olefins.

4. The process as in claim 1, wherein subjecting the mixture of solvent and deasphalted residual oil to fluidized catalytic cracking reactions occurs in a downflow fluid catalytic cracking unit.

5. The process as in claim 4, wherein the reaction temperature in the fluid catalytic cracking unit is about 500°C to about 650°C.

6. The process as in claim 4, wherein the reaction pressure in the fluid catalytic cracking unit is about 1 Kg/cm2 to about 5 Kg/cm2.

7. The process as in claim 4 wherein contact time between reactants and catalyst in the fluid catalytic cracking unit is about 0.1 seconds to about 10 seconds.

8. The process as in claim 4 wherein a catalyst to feed ratio in the fluid catalytic cracking unit is about 2:1 to about 40:1.

9. The process as in claim 1, in which a portion of the C5 and lower components of the mixture of solvent and deasphalted residual oil are removed prior to fluidized catalytic cracking reactions.

10. The process as in claim 9, wherein a portion of the removed C5 and lower components are recycled as a at least a portion of solvent for the step of mixing the residual oil feedstream with the solvent.

11. The process as in claim 1, wherein the solvent in the step of mixing the residual oil feedstream is naphtha or natural gas condensate of carbon range starting at C5 or above.

12. The process as in claim 1, wherein the solvent in the step of mixing the residual oil feedstream is a light portion of an initial light stream, and a heavy portion of the initial light stream is admixed with the mixture of solvent and deasphalted residual oil for fluidized catalytic cracking reactions.

13. The process as in claim 12, wherein the initial light stream is naphtha or natural gas condensate of carbon range starting at C5 or above.

14. The process as in claim 1, wherein the residual oil in the step of mixing the residual oil feedstream is a heavy portion of an initial heavy stream, and a light portion of the initial heavy stream is admixed with the mixture of solvent and deasphalted residual oil for fluidized catalytic cracking reactions.

15. The process as in claim 1, wherein the residual oil feedstream is a straight run residue obtained from atmospheric distillation and/or vacuum distillation.

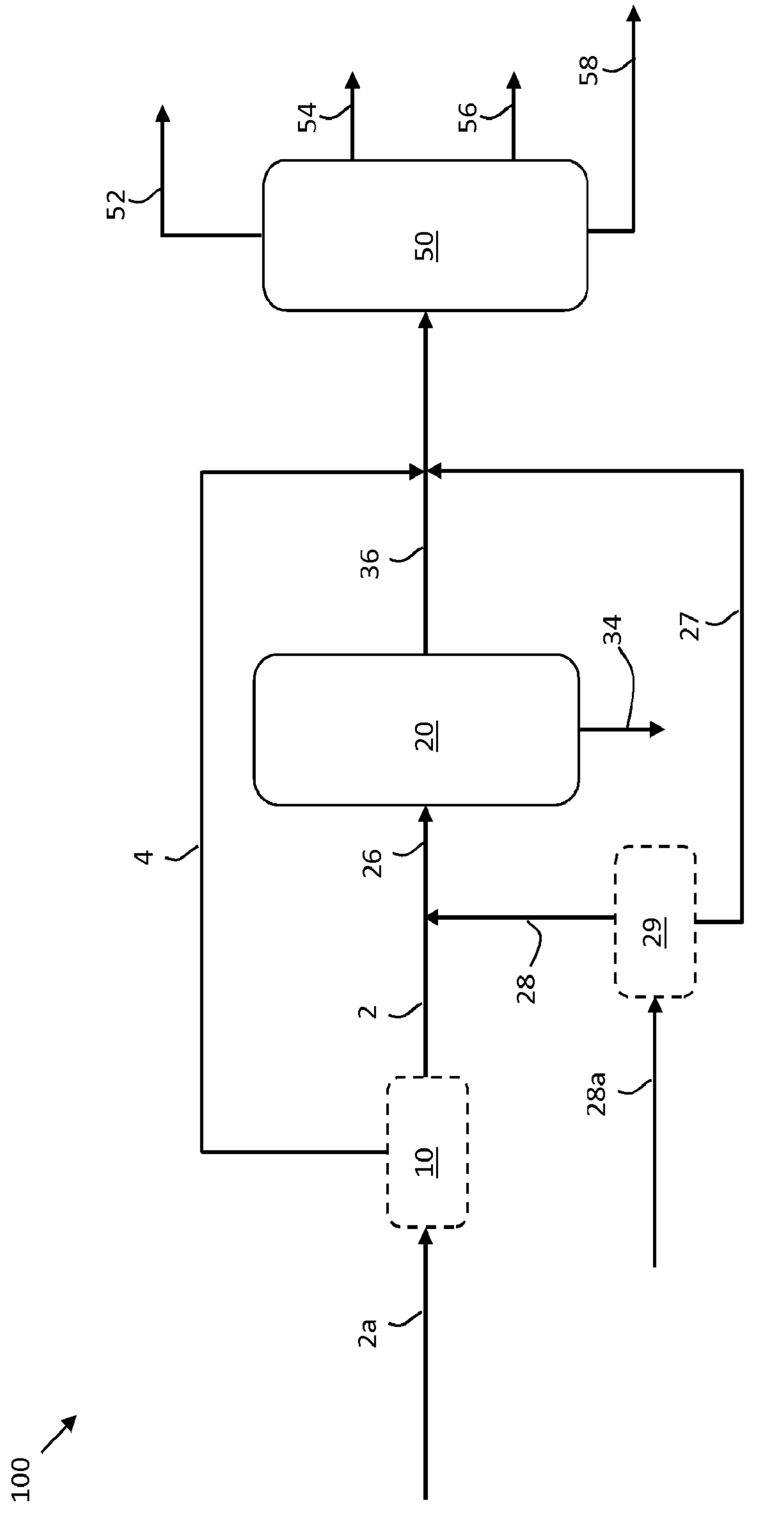

FIG. 1

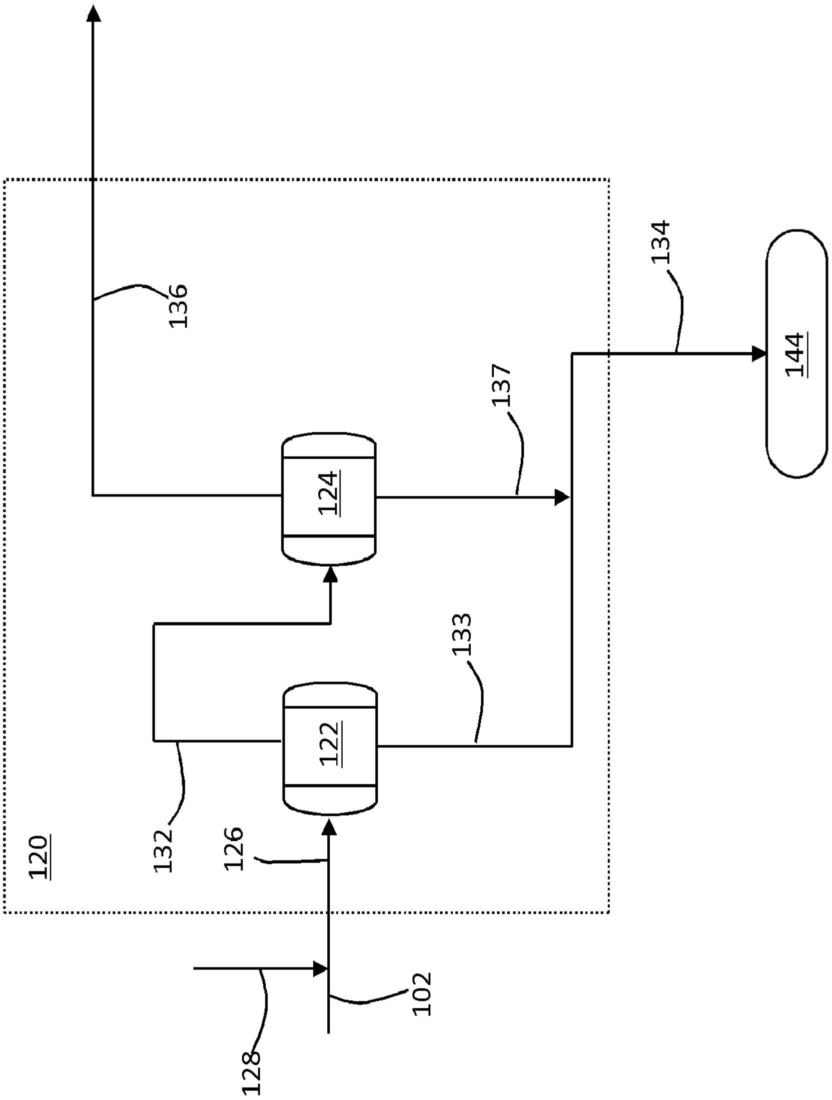

FIG. 2

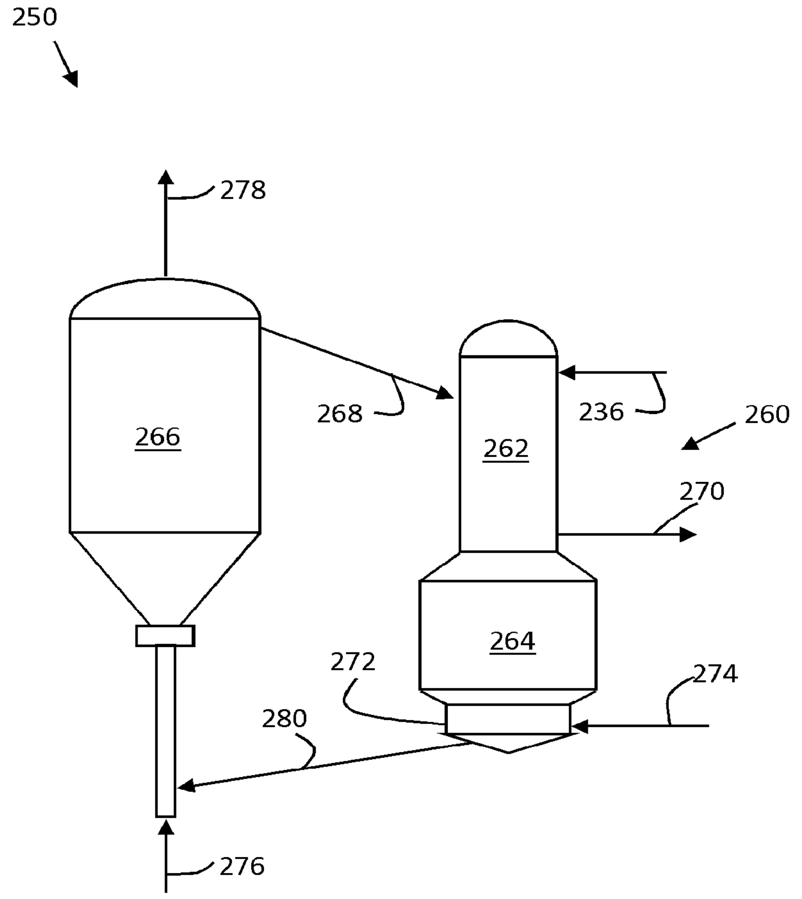
250
278
266
268
262
236
260
270
264
272
274
280
276

FIG. 3

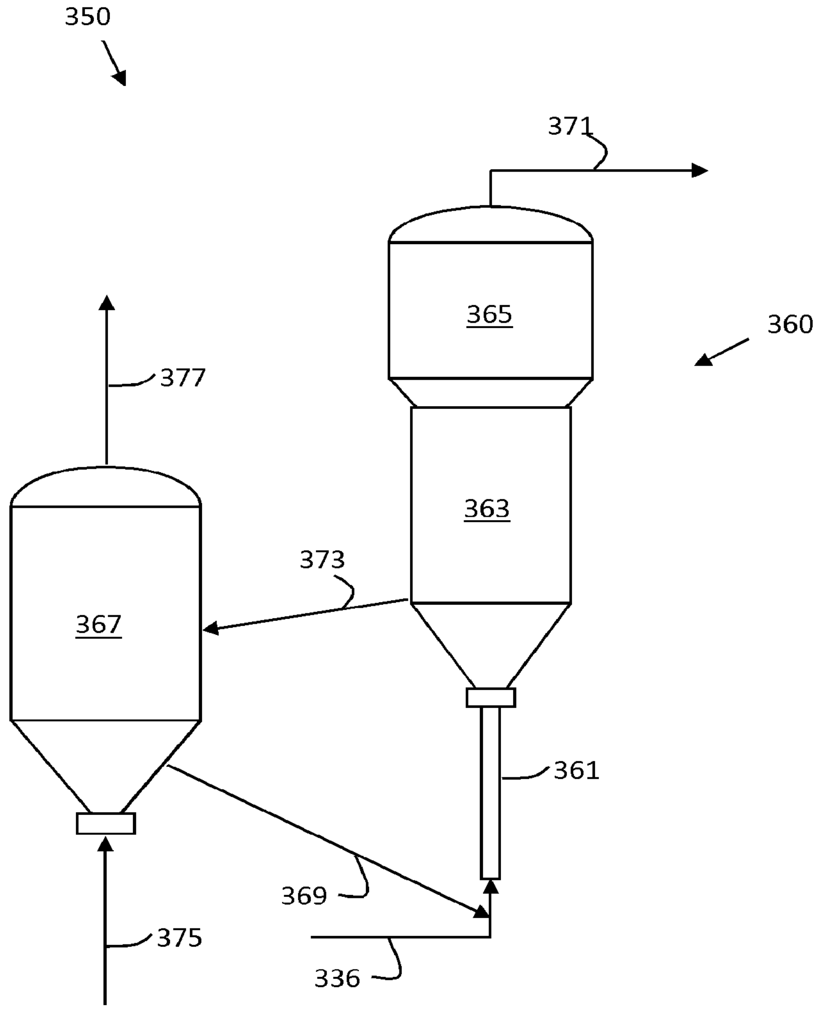
350
371
365
360
377
363
373
367
361
369
375
336

FIG. 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/068034

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10G55/06 C10G11/18 C10G21/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	NL 79 903 C (N.V. DE BATAAFSCHE PETROLEUM MAATSCHAPPIJ) 15 December 1955 (1955-12-15) claims 1,4; examples 1,2; tables 2,4 -----	1-15
X	US 5 000 838 A (BARTILUCCI MARK P [AU] ET AL) 19 March 1991 (1991-03-19) cited in the application column 3, line 6 - line 9; claim 10 column 6, line 61 - line 64 -----	1-15
X	US 3 628 975 A (POOL JOE VAN) 21 December 1971 (1971-12-21) figure 1 ----- -/--	1-5

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 26 February 2015	Date of mailing of the international search report 06/03/2015
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Deurinck, Patricia

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/068034

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 686 028 A (VAN DRIESEN ROGER P [US] ET AL) 11 August 1987 (1987-08-11) column 3, lines 31-34,50-59; claim 1; figure 1 -----	1-15
A	US 6 190 536 B1 (LOKHANDWALA KAAEID A [US] ET AL) 20 February 2001 (2001-02-20) column 1, line 16 - line 53 column 4, line 30 - line 35 column 7, line 44 - column 9, line 16 -----	1-15

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2014/068034

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
NL 79903	C	15-12-1955	NONE	
US 5000838	A	19-03-1991	NONE	
US 3628975	A	21-12-1971	NONE	
US 4686028	A	11-08-1987	NONE	
US 6190536	B1	20-02-2001	NONE	