

**INTEGRATED PROCESS FOR DEASPHALTING AND
DESULFURIZING WHOLE CRUDE OIL**

RELATED APPLICATION

[01] This application claims priority from U.S. Provisional Patent Application No. 61/655,732 filed June 5, 2012, incorporated by reference in its entirety.

FIELD OF THE INVENTION

[02] The invention relates to an integrated process for treating whole crude oil to remove asphalt and other impurities therefrom. To elaborate, the integrated process comprises the steps of separating asphalt from the whole crude oil, followed by treating the deasphalted oil via hydrotreatment/hydrocracking with a catalyst, to remove materials such as sulfur and nitrogen. In parallel, the recovered, asphalt containing fraction can be gasified, to produce hydrogen that is then used in the hydrocracking step.

BACKGROUND AND PRIOR ART

[03] Conventional processes for treating crude oil involve distillation, and then various cracking, solvent refining, and hydroconversion processes, so as to produce a desired group of products, such as fuels, lubricating oil products, petro-chemicals, chemical feedstocks, and the like. An exemplary process includes the distillation of the crude oil in an appropriate atmospheric distillation column, resulting in gas oil, naphtha, other gases, and atmospheric residuum. This last portion is fractionated further in a vacuum distillation column, so as to produce so-called vacuum gas oil, and vacuum residuum. The vacuum gas oil, in turn, is usually cracked via fluid catalytic cracking or hydrocracking, to produce more valuable light transportation fuel products, while the residuum can be processed further, to yield additional useful products. The methods involved in these processes can include, e.g., hydrotreating or fluid catalytic cracking of the residuum, coking, and solvent deasphalting. Any materials recovered from crude distillation at fuel boiling points have typically been used, directly, as fuels.

[04] To elaborate on the processes described, supra, solvent deasphalting is a physical, separation process, where feed components are recovered in their original states, i.e., they do not

undergo chemical reactions. Generally, a paraffinic solvent, containing 3-8 carbon molecules, is used to separate the components of the heavy crude oil fractions. It is a flexible process, which essentially separates atmospheric, and vacuum heavy residues, typically into two products: (i) asphalt and (ii) deasphalted or demetallized oil, referred to as "DAO" or "DMO," respectively hereafter. The choice of solvent is left to the skilled artisan, and is chosen with desired products, yields, and quantities in mind, as are other process parameters, such as the operating temperature, and the solvent/oil ratio. As a general rule, as the molecular weight of the solvent increases, so does solubility of the oil into the solvent. For example, either propane or a propane/isobutane mixture is typically used to manufacture lube oil bright stock. If, on the other hand, the DAO will be used in conversion practices, like fluid catalytic cracking, solvents with higher molecular weights (e.g., butane or pentane, or mixtures thereof), are used. The products of DAO solvation include those described supra, as well as lube hydrocracking feed, fuels, hydrocracker feed, fluid catalytic cracking feed, or fuel oil blends. The asphalt product may be used as a blending component for various grades of asphalt, as a fuel oil blending component, or as a feedstock for heavy oil conversion units (e.g., cokers.)

[05] Conventional solvent deasphalting methods are carried out without catalysts or adsorbents. U.S. Patent No. 7,566,394, the disclosure of which is incorporated by reference, teaches improved solvent deasphalting methods which employ solid adsorbents. The improvement in the methodology leads to separation of nitrogen and polynuclear aromatics from DAO. The adsorbents are then removed with the asphalt products, and are either sent to an asphalt pool, or gasified in a membrane wall gasifier, where solids are required.

[06] Hydrocracking processes, as is well known, are used commercially in many refineries. A typical application of a hydrocracking process involves processing feedstreams which boil at 370°C to 520°C in conventional units, and those which boil at 520°C and above, in so-called "residue units." Simply stated, hydrocracking is a process by which C-C bonds of large molecules in a feedstream, are broken, to form smaller molecules, which have higher volatility and economic value. In addition, hydrocracking processes typically improve the quality of hydrocarbon feedstock, by increasing the H/C ratio by hydrogenation of aromatic compounds, and by removing organo-sulfur, and organic nitrogen compounds.

[07] Given the significant economic benefits that result from hydrocracking, it is not surprising that there have been substantial developments in improving hydrocracking processes, and the development of more active catalysts.

[08] In practice, hydrocracking units usually include two principal zones: a reaction zone and a separation zone. There are also three standard configurations: single stage, series-flow (“once-through”), with and without recycling, and two stage processes, with recycling. The choice of reaction zone configuration depends upon various parameters, such as feedstock quality, the product specification and processing objectives, and catalyst selection.

[09] Single stage, once-through hydrocracking processes are carried out at operating conditions which are more severe than typical hydrotreating processes, but which are less severe than conventional full pressure hydrocracking processes. Mild hydrocracking is more cost effective than more severe processes but, generally, it results in production of lesser amounts of desired middle distillate products, which are of lower quality than the products of conventional hydrocracking.

[10] Single or multiple catalyst systems can be used depending upon, e.g., the feedstock processed and product specifications. Single stage hydrocracking units are generally the simplest configuration, designed to maximize middle distillate yield over a single or dual catalyst system. Dual catalyst systems are used in stacked-bed configurations or in two different reactors.

[11] Feedstock is typically refined over one or more amorphous-based hydrotreating catalysts, either in the first catalytic zone in a single reactor, or in the first reactor of a two-reactor system. The effluents of the first stage are then passed to the second catalyst system which consists of an amorphous-based catalyst or zeolite catalyst having hydrogenation and/or hydrocracking functions, either in the bottom of a single reactor or the second reactor of a two-reactor system.

[12] In two-stage configurations, which can also be operated in a “recycle-to-extinction” mode of operation, the feedstock is refined by passing it over a hydrotreating catalyst bed in the first reactor. The effluents, together with the second stage effluents, are passed to a

fractionator column to separate the H_2S , NH_3 , light gases (C_1 - C_4), naphtha and diesel products which boil at a temperature range of 36-370 °C. The unconverted bottoms, free of H_2S , NH_3 , etc. are sent to the second stage for complete conversion. The hydrocarbons boiling above 370 °C are then recycled to the first stage reactor or the second stage reactor.

[13] Hydrocracking unit effluents are sent to a distillation column to fractionate the naphtha, jet fuel/kerosene, diesel, and unconverted products which boil in the nominal ranges of 36-180 °C, 180-240 °C, 240-370 °C and above 370 °C, respectively. The hydrocracked jet fuel/kerosene products (i.e., smoke point >25 mm) and diesel products (i.e., cetane number >52) are of high quality and well above worldwide transportation fuel specifications. While hydrocracking unit effluents generally have low aromaticity, any aromatics that remain will lower the key indicative properties of smoke point and cetane numbers for these products.

[14] One major technical challenge posed in hydrotreating and/or hydrocracking heavy oil fractions or whole crude is the effect of small concentrations of contaminants, such as organic nickel or vanadium containing compounds, as well as poly nuclear aromatic compounds. These organometallic compounds, and others, reduce the activity or lifetime of hydrotreating catalysts. The contaminants and polynuclear aromatics cause reduced process performance, a need for increased capital, and operating costs of refinery processing units. The metals in the residual fraction of the crude oil deposit on the hydroprocessing catalyst pores and results in catalyst deactivation. These problems are addressed and solved in the disclosure which follows.

[15] Conventional, prior art processes in the field of the invention involve distillation of crude oil, followed by treatment of the light fractions (naphtha and diesel fuel) which remain following distillation. These light fractions are desulfurized and/or treated (i.e., "reforming" in the case of naphtha) to improve their quality, and are then sent to fuel pools for further use. The vacuum residuum, referred to supra, is treated via solvent deasphalting, so as to secure deasphalted oil and asphalt. Asphalt is then further treated, by being gasified, or it is sent to the "asphalt pool."

[16] Prior art processes show the treatment of fractionates or distillates of crude oil, rather than treatment of crude oil per se, as in accordance with the invention. See, e.g., PCT/EP2008/005210 where distillates are used to produce asphaltenes and DAO; U.S. Patent

No. 3,902,991, wherein a vacuum residuum is solvent extracted followed by hydrocracking and gasification of the DAO and asphalt; published U.S. Patent Application 2011/0198266, showing treatment of a vacuum residue; published U.S. Patent Application 2008/0223754, where residues from a distillation process are used to manufacture asphaltene and DAO; and EP 683 218, which also teaches treating residual hydrocarbon products. Also see, e.g., U.S. Patent Nos. 8,110,090; 7,347,051; 6,357,526; 6,241,874; 5,958,365; 5,384,297; 4,938,682; 4,039,429; and 2,940,920, as well as Published U.S. Patent Application 2006/0272983; PCT/KR2010/007651, European Patent Application 99 141; and Published Japanese Patent Application 8-231965. All references discussed herein are incorporated by reference in their entirety.

[17] The current invention simplifies and improves the prior art process, by eliminating the need for distillation, and for treating the naptha and diesel fractions. Rather, the invention, as will be seen, simplifies whole crude oil processing by hydrocracking the whole stream, and eliminating the steps referred to supra.

[18] How the invention is achieved will be seen in the disclosure which follows.

BRIEF DESCRIPTION OF THE DRAWING

[19] Figure 1 shows a schematic depiction of the process of the invention, suing a single reactor embodiment.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[20] The invention may be best understood by referring to Figure 1, which illustrates the general method of the invention as well as a system used in its practice.

[21] Referring to Figure 1, a feedstream of crude oil "10" is added to a reaction chamber "11," so as to solvent deasphaltize it, thereby producing an asphalt fraction "12," and a fraction of deasphalted oil, or "DAO 13" as referred to supra. The manner in which this fractionation can be accomplished is described, supra, i.e., a paraffinic solvent containing one or more carbon atoms containing from 3-8 carbons, is used. No catalyst or adsorbent is necessary; however, see U.S. Patent No. 7,566,394, incorporated by reference, supra, teaching an improved deasphalting process using a sorbent. No distillation is used, nor are the light components separated.

[22] The "DAO" "13" is transferred to a hydrocracking / hydrotreating zone "14." It is to be understood that, while Figure 1 describes a single reactor, the various methods for hydrocracking, including "once through, series flow," and "two-stage" reactions, may all be used. The reactor contains one or more catalysts which remove heteroatoms, such as sulfur and nitrogen from the DAO. Such catalysts are well known to the art, and are not repeated herein. Exemplary of such are catalysts described in, e.g., PCT/US11/46272 filed August 2, 2011 and incorporated by reference herein. The cracking reaction takes place in the presence of hydrogen, which is supplied as explained infra.

[23] It will be recalled that in addition to the DAO, solvent deasphalting of the crude oil produces an asphalt fraction "12." This asphalt fraction is transferred to a gasification chamber "15," together with oxygen "16" and steam "17." These components, i.e., the oxygen and steam, may be supplied in pure form, or via, e.g., atmospheric air. The asphalt, oxygen and steam are combined, at temperatures and pressures which result in production of hydrogen. In the depicted embodiment, this hydrogen "18," is channeled to the DAO hydrocracking unit "14," to supply the hydrogen necessary for the hydrocracking process to take place. (It should be noted that the gasification of asphalt is an optional step, and may be replaced via, e.g., supplying an independent source of hydrogen). Various products, e.g., gases 19, and upgraded crude oil 20, result, and products of gasification 21 are used in the generation of electricity or for other uses.

[24] By separating the asphalt component of the crude oil from the DAO, one eliminates problems such as the failing of catalysts by metals that are present in the asphalt fraction. Catalyst life cycles are increased, and the need for shut downs of reactors, and replacement of materials, are decreased.

[25] In the process as described herein, the hydrocracking process takes place at standard hydrocracking conditions, i.e., pressures ranging from about 100 to about 200 bars, temperatures ranging from about 350°C (to about 450°C, LHSVs of between 0.1 and 4.0 h⁻¹, and hydrogen oil ratios of from about 500 to about 2,500 SLt/Lt.

EXAMPLE

[26] This example describes an embodiment of the invention in which gasification of the “SDA” fraction was used to produce hydrogen, which was then used in the hydrocracking of the DAO fraction. It will be understood that the H_2 may be supplied via other means.

[27] A 1000 kg sample of crude oil was solvent deasphalted, using art known techniques, with butane solvents and adsorbents, in a reaction chamber, such as is depicted by “11” in Figure 1. Prior to deasphalting, the crude oil was analyzed, and the results of this analysis are presented in the Table, column 1, which follows.

[28] Following deasphalting, the asphalt fraction and deasphalted oil, or “DAO,” were also analyzed, and these results are presented in columns 2 and 3 of the Table.

[29] The asphalt fraction was gasified by oxygen and steam combining it into membrane wall reactor or gasification chamber, depicted at “14” in Figure 1. The mixture was heated to 1045°C, with a water to carbon ration of 0.6 (in terms of weight), and an oxygen:pitch ratio of 1.0.

[30] After gasification was completed, the raw syngas product was combined with steam that was produced by either a boiler or process heat exchanger to a water gas shift (“WGS”) reactor, which was operated at 318°C, one bar of pressure, and a water to hydrogen ratio of 3. This increased hydrogen yield.

[31] All analyses and results are presented in the table which follows and which is elaborated upon infra:

Table : Summaries of Components

Column #		1	2	3	4	5	6	7	8
Stream#		10	13	12	19	20	16	17	18
Stream Name		Arab Heavy CO	Deasphalted Crude Oil	Asphalt	C1-C4	Upgraded Crude Oil	Oxygen	Steam	Hydrogen
Feedrate	kg	1000	922	78	4.8	930	78	46.8	13
Density	Kg/Lt	0.8904	0.876	1.210		0.825			
API Gravity	°	27.4	30.0	-14.6		40.1			
Carbon	W%	84.8233	85.04	78.36					
Hydrogen	W%	12.18	12.83	6.43					
Sulfur	W%	2.837	1.99	10.79		<20			
Nitrogen	ppmw	1670	535	9575		<20			
MCR	W%	8.2	2.55	61.3					
Nickel	ppmw	16.4	1	582		<1			
Vanadium	ppmw	56.4	1	172		<1			
C5-Asphaltenes	W%	7.8							
C7-Asphaltenes	W%	4.2							
Toluene insolubles	W%	0.0008							
Ashes	W%	0.014							
H2	W%								99.5
H2S	W%					2.47			
NH3	W%					0.11			
C1-C4	W%				100				
36-190	W%	17.4	20.6			21.5			
190-370	W%	25.8	29.0			36.0			
370-490	W%	17.9	19.1			21.2			
490+-	W%	39.0	31.3			21.2			

[32] While gasification was taking place, the DAO portion was introduced to a standard, hydrocracking unit, shown in "14," and hydrocracked at 360°C, 115 bars of hydrogen partial pressure, with an overall liquid hourly space velocity of 0.3h^{-1} , with a Ni-Mo promoted, amorphous VGO hydrocracking catalyst and a VGO zeolite catalyst, at a loading ratio of 3:1. See PCT/US11/46272, incorporated supra, for the catalyst used herein.

[33] The products which left the hydrocracking chamber were analyzed for content of low molecular weight hydrocarbons ($\text{C}_1\text{-C}_4$), upgraded crude oil, oxygen, steam, and hydrogen. These values are presented in columns 4-5 in the Table. The upgraded crude oil was also analyzed for various minor components, as well as boiling fractions, in the same way the crude oil, and DAO were analyzed. To elaborate upon the Table, Column 1 presents the analysis of the

crude oil ("CO") used in the reaction. Column 2 is the analysis of the resulting DAO and Column 3, the asphalt fraction. Column 4 presents the information on the gas produced in the hydrocracking step, with Column 5, the upgraded crude oil. Finally, Columns 6, 7, and 8 refer to the reactants added to the reactors, as discussed supra.

[34] The foregoing disclosure sets forth the features of the invention, which is a simplified methodology for reducing impurities, such as sulfur and nitrogen, in a feedstock, such as crude oil, which does not involve distillation. To summarize, the crude oil is solvent deasphalted, resulting in DAO and asphalt. The DAO is then hydrocracked in the presence of a catalyst so as to desulfurize and denitrogenize it, and to convert any hydrocarbons which have a boiling point over 370°C into distillates. Concurrently, the asphalt fraction is gasified so as to produce hydrogen. In one embodiment, the hydrogen is channeled back into the hydrocracking reactor and used in that process. The nature of the feedstock will, of course vary and may include ash in an amount ranging from about 2% to about 10% of the total feedstock. The feedstock may be liquid or solid. Liquid feedstocks having components with boiling points of from about 36°C to about 2000°C are preferred. The feedstock may be, e.g., bituminous, oil, sand; shale oil, coal, or a bio liquid, and preferably contains less than 20 ppmw of sulfur.

[35] In practice, it is desirable to subject the crude oil to a paraffinic solvent to separate DAO and asphalt. The solvent comprises one or more C₃ - C₇alkanes, which may be straight chained or branched. Preferably, the solvent comprises one or, most preferably, a mixture of butanes. Solvation takes place at temperatures and pressures, which are below the critical values for both of these.

[36] It is especially preferred to carry out the deasphalting step, discussed, in the presence of a solid adsorbent, preferably added in an amount sufficient to provide a hydrocarbon:adsorbent ratio of from 20:0.1 to 10:1, expressed in terms of W/W.

[37] After separation, the DAO is transmitted to a hydrocracking unit, where hydrocracking is carried out at conditions which may vary, but are preferably a pressure of from about 100 to about 200 bars, a temperature of from about 350°C to about 500°C, an LHSV of from about 0.1 to about 4.0 h⁻¹, and a hydrogen:oil ratio of from about 500 to about 2500 SL/L.

Any standard hydrocracking system may be used including single reactors, multiple reactors operated in series, fixed bed reactors, ebullated bed reactors, and so forth.

[38] A catalyst is used in the hydrocracking process, preferably the catalyst incorporated by reference supra. Preferably, the catalyst contains from about 2% to about 40% by weight of active metal, a total pore volume of from about 0.3 to about 1.5 cc/g, a total surface area of from about 200 to about 450 m²/g, and an average pore diameter of at least 50 angstroms.

[39] With respect to the active metal, referred to supra, metals from Group VI, VII or VIIIB are preferred, and may include one or more of Co, Ni, W, and Mo. While it is not required to do so, the catalysts are generally incorporated on a support, such as alumina, silica, a zeolite or a zeolite modified by, e.g., steam, ammonia, acid washing and/or insertion of transition metals into its structure.

[40] Concurrent with the hydrocracking of the DAO, the asphalt portion of the crude oil is gasified in a gasification chamber, e.g., a membrane wall type reactor, preferably at a temperature of from about 900°C to about 1700°C, and a pressure of from about 20 bars to about 100 bars. Gasification takes place in the presence of an O₂ containing gas, which may be, e.g., pure O₂ or more preferably, atmospheric gas. Means may be provided to control the amounts of asphalt and oxygen entering the gasification reactor. Such means are well known to the skilled artisan and need not reiterated here. It is preferred to control the amounts of asphalt and O₂, so that a stoichiometric balance permitting partial combustion ensues. This can be determined via determining the hydrocarbon content of the crude oil, such as was done in the example, supra. Preferably, the amounts are selected such that the oxygen:carbon ratio ranges from about 0.2:1.0 to about 5:0.1 by weight.

[41] Optionally, steam may be added to the gasification chamber. When it is, it too is added in an amount based upon the carbon content of the crude oil, and is preferably presented at a ratio of from about 0.1:1.0 to about 100:1.0 by weight. Gasification results in a product sometimes referred to as "syngas" consisting essentially of hydrogen and carbon monoxide. In one embodiment of the invention, the syngas produced by gasification is transmitted to a water gas shift reaction chamber and treated to produce H₂ and CO₂, after which H₂ is separated. The resulting, pure H₂ may be channeled to the hydrocracking reaction.

[42] The process by which the syngas is treated may include treatment at a temperature of from about 150°C to about 400°C, and a pressure of from about 1 to about 60 bars.

[43] As was seen, supra, gas content can be measured at any point in the process described here. Hence, following measurement of CO content in the syngas, water can be added to the reaction chamber, preferably at a molar ratio with CO of from about 3:1 to about 5:1.

[44] Other facts of the invention will be clear to the skilled artisan and need not be reiterated here.

[45] The terms and expression which have been employed are used as terms of description and not of limitation, and there is no intention in the use of such terms and expression of excluding any equivalents of the features shown and described or portions thereof, it being recognized that various modifications are possible within the scope of the invention.

CLAIMS

1. A method for reducing impurities in a hydrocarbon containing feedstock, comprising:
 - (i) solvent deasphalting said feedstock in the presence of a solid adsorbent which contacts said feedstock, to produce an asphalt fraction and deasphalted oil (DAO), in a first reaction chamber,
 - (ii) processing said DAO and said asphalt fraction in separate, second and third reaction chambers;
 - (iii) hydrocracking said DAO in said second reaction chamber to remove sulfur and nitrogen therefrom and to distillate any hydrocarbons contained in said DAO which have a boiling point over 370°C; and
 - (iv) gasifying said asphalt fraction via combining it with oxygen and steam in said third reaction chamber, to produce hydrogen therefrom.
2. The method of claim 1, comprising introducing said hydrogen produced in said third reaction chamber into said second reaction chamber.
3. The method of claim 1, wherein said solvent deasphalting comprises mixing said crude oil with a solvent containing C₃-C₇ carbon atoms, at a temperature and a pressure below critical temperature and critical pressure of said solvent.
4. The method of claim 3, wherein said solvent comprises n-butane and isobutane.
5. The method of claim 3, comprising mixing said crude oil and solvent at a temperature and pressure below the critical temperature and critical pressure of said solvent.
6. The method of claim 3, wherein said crude oil and solvent are combined at a weight ratio of from 10:1 to 200: 1 w/w.
7. The method of claim 1, comprising hydrocracking said DAO at a pressure of from 100 - 200 bars, a temperature of from 350°C to 500°C, an LHSV of from 0.1 to 4.0 h⁻¹, and a hydrogen:DAO ratio of from 500 to 2,500 SL/Lt.
8. The method of claim 1, comprising hydro cracking said DAO in a series of multiple chambers.
9. The method of claim 1, wherein said hydrocracking chamber is a fixed bed, ebullated bed, or slurry bed chamber.
10. The method of claim 1, comprising hydrocracking said DAO in the presence of a catalyst, which contains from 2-40 wt% active metal, a pore volume of from 0.33-1.50 cc/gm, a surface area of 250 - 450 m²/g, and an average pore diameter of at least 50 Angstroms.
11. The method of claim 10, wherein said active metal is a Group VI, VII, or VIII B metal.
12. The method of claim 10, wherein said active metal comprises Co, Ni, W, or Mo.
13. The method of claim 10, wherein said catalyst is presented on a support.
14. The method of claim 13, wherein said support comprises alumina, silica, or a zeolite.
15. The method of claim 14, wherein said support is a zeolite.
16. The method of claim 15, wherein said zeolite has been modified by treatment with at least one of steam, ammonia, or acid, and contains at least one transition metal.

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17. The method of claim 16, wherein said at least one transition metal is Zn or Ti.
 18. The method of claim 1, comprising gasifying said asphalt fraction at a temperature of from 900°C to 1700°C, and a pressure of from 20 bars to 100 bars.
 19. The method of claim 1, further comprising adjusting the amount of asphalt and at least one of oxygen and steam in said third reaction chamber to provide a stoichiometric balance therebetween which results in partial combustion of said asphalt.
 20. The method of claim 18, wherein said stoichiometric ratio based on the oxygen:carbon ratio is from 0.2: 1:0 to 10:0.2 by weight.
 21. The method of claim 18, comprising introducing asphalt and steam to said third reaction chamber in a ratio of from 0.1 to 1.0 to 10:0.1 based upon weight of carbon in said crude oil.