

**METHOD FOR ENHANCED UPGRADING OF
HEAVY OIL BY ADDING A HYDROTREATING
STEP TO AN UPGRADING PROCESS**

RELATED APPLICATIONS

[001] This application claims priority from U.S. Provisional Application No. 61/908,345 filed November 25, 2013, incorporated by reference in its entirety.

FIELD OF THE INVENTION

[002] This invention relates to an improvement in methods for processing heavy oils to convert them into useful, lighter products. More particularly, it relates to a method for improving a catalytic hydrothermal aquathermolysis process, by adding a hydrotreating step to the process.

BACKGROUND AND PRIOR ART

[003] Residual and heavy hydrocarbon oils contain heteroatoms, heavy aromatic molecules, and asphaltenes, all of which adversely impact the potential of these starting materials to be upgraded to more valuable, lighter products.

[004] Thermal cracking of heavy oil has been used, worldwide, (i) to crack these heavy oils to obtain lighter products, and to reject carbon in the form of coke, or (ii) to decrease the viscosity of the heavy oils for transportation. There are a variety of thermal processes available; including delayed coking, fluid coking, and thermal coking.

[005] Delayed coking, which is a well-known technique, uses thermal decomposition of heavy liquid hydrocarbons to produce coke, gas, and liquid products at different boiling temperature ranges. The resulting coke is generally treated as a low value by-product, and is recovered or not, depending on its quality.

[006] Thermal cracking is a mild, thermal cracking process, used to lower the viscosity of heavy oils. The degree of conversion of the starting material, however, is compromised by low asphaltene stability limits.

[007] Other conversion processes used to secure materials of higher value include Residue Fluid Catalytic Cracking (RFCC), and hydrocracking. RFCC, however, is limited in its ability to tolerate high Conradson Carbon Residue (CCR), asphaltenes and metal content in feedstocks. Hydrocracking requires a high hydrogen supply, in order to maintain high hydrogen partial pressures. Hence, there is a need to find new, economical methods for increasing the upgradeability and/or quality of heavy petroleum oils.

[008] The upgrading of heavy oil is dependent on three factors: (i) the type or origin of the heavy oil, (ii) its composition (e.g., asphaltene and polycyclic aromatic content), and the technology used. Of these, only technology is under the control of the investigator.

[009] As noted, supra, different technologies are used, in a number of applications, but they are limited in their usefulness in that their conversion rates are low, they involve high operating costs, and/or they produce large amounts of by-products, such as coke, which are expensive to dispose of properly.

[0010] Processes for upgrading heavy oils via catalytic hydrothermal aquathermolysis is a known technology. It results in better conversion rates, and lower costs to implement, as compared to other processes.

[0011] The invention involves an improvement to this known process in that a hydrotreating step is added. The addition of this step allows the artisan to increase upgrade process severity, improve product yields and quality, and provides a source of hydrogen for the entire process.

SUMMARY OF THE INVENTION

[0012] The invention relates to a method for processing heavy oils in a catalytic, aquathermolysis process, wherein the process further comprises hydrotreating the starting material. The process requires the use of a catalyst, and the hydrotreating step is carried out at conditions which include temperatures ranging from about 300 °C to about 500 °C, preferably from 380 °C to 450 °C and pressures ranging from about 50 kg/cm² to about

100 kg/cm² or from about 1 to about 200 Bar, preferably from about 50 Bar to about 180 Bar.

BRIEF DESCRIPTION OF THE FIGURE

[0013] Figure 1 shows an embodiment of the invention where hydrotreating takes place downstream of a feedstock preparation unit.

[0014] Figure 2 shows an embodiment where the hydrotreating takes place upstream of the feedstock preparation unit.

[0015] Figure 3 shows an embodiment of the invention where hydrotreating takes place downstream of the upgrading unit.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0016] With reference to Figure 1, the feedstock/catalyst preparation unit consists of the vessels 102, 107 and 109 as shown in Figure 1. There, the heavy oil is mixed with an upgrading metallic catalyst precursor, water and hydrogen, and then heated in a furnace and sent to the decomposition reactor 108 to form the catalytic suspension. A feedstock 101, having a boiling point greater than about 300 °C is added to a mixer 102, which contains a catalyst together with aromatic rich hydrocarbons 103, metal containing catalyst precursors 104, and water 105. This results in a catalytic slurry emulsion 106, which is heated via heater 107, and then moves to a decomposition reactor 108 operated at 300-500 °C. At this point the catalyst is formed and the mixture is referred to as a catalytic suspension. After this, the catalytic suspension is routed to a low pressure separator 109. The bottom product from the low pressure separator is then preheated in the preheater 110, before entering into a hydrotreater 111, where the hydrogenation step occurs, using hydrogen 112 and the hydrotreating catalyst. The resulting, hydrotreated effluent is separated in a fractionation zone 113 such that unreacted hydrogen is recycled to the hydrotreater, contaminant gases such as H₂S and NH₃ are separated, while low weight materials, e.g., C₁-C₄ hydrocarbons such as naphtha which boil at a temperature of 36-180 °C, and hydrocarbons which boil at gas oil range (180-375 °C), are sent to a light products recovery unit, while heavier bottom products are mixed with water to form a

slurry, optionally with hydrogen, and moved to a reactor 114 where catalytic hydrothermal aquathermolysis takes place, i.e., further upgrading of the heavy oil. This can be done via, e.g., thermal and/or catalytic cracking.

[0017] The upgraded oil is then dispatched to a fractionator 115, where light weight fractions are removed, unconverted heavy oils are then recycled back to the mixer 102, while the light gases, hydrocarbons which boil in naphtha (at 36-180 °C), and gas oil range (180-375 °C), are sent to the light product recovery unit. The fractionator may include multiple vessels to separate gas, liquid and aqueous phases.

[0018] A further embodiment of the invention is shown in Figure 2, which shows a feedstock 201, also having a boiling point above 300 °C, which is introduced, together with hydrogen 202, into a hydrotreating reactor 203, which contains a hydrotreating catalyst. Action of the catalyst on the mixture of feedstock and hydrogen results in a first effluent. This effluent moves to a fractionator 204, where contaminant gases like H₂S and NH₃, light gases (C₁-C₄ gases), hydrocarbons boiling in naphtha range (36-180 °C) and in gas oil range (180-375 °C), are separated, 205. The heavy bottoms, 206 are passed to a feedstock/catalyst preparation unit 207. The catalytic suspension from the feedstock/catalyst preparation unit 207 is then heated and sent to the upgrading reactor 208 (the catalytic hydrothermal aquathermolysis reactor). The reactor effluent is sent to the fractionator 209 to separate the light fractions produced in the prior step (i.e., waste gases, light gases, naphtha and gas oil fractions). The unreacted materials can be recycled to the hydrotreatment reactor, for further upgrading cycles. The fractionation zone can include multiple vessels to separate gas, liquid and aqueous phases.

[0019] In Figure 3, one sees an embodiment of the invention where a hydrotreating unit is downstream of an upgrading unit. As in the other two embodiments, hydrocarbons having a boiling point above 300 °C, 301, are mixed with upgrading catalysts in a feedstock/catalyst preparation unit 302, and then sent to a heater and decomposition reactor to produce the catalytic suspension, which is then heated in the charge heater. The heated feedstock is then sent to the upgrading reactor 303 (the catalytic hydrothermal aquathermolysis zone for upgrading via further cracking. The

upgraded oil is then sent to a fractionator zone 304, which separates light products described in embodiments 1 and 2, supra, while the heavy bottom is sent to a hydrotreater 306, which contains a hydrotreating catalyst. The resulting hydrotreated effluent is sent to a fractionator zone 305, where light materials are separated, and the unconverted oil is recycled back to feedstock preparation unit 302 for further upgrading cycle. The fractionation zones may include multiple vessels to separate gas, liquid and aqueous phases.

[0020] In all embodiments, the hydrotreating reactor, can be, e.g., a fixed bed, ebullated bed, moving bed, slurry, or CSTR.

[0021] Every reactor described herein may be single or multiple, depending upon the composition of the feedstock, the nature of contaminant, and/or the specification of the desired product. As an example, if the feedstock metal content is high, a separate reactor is used to remove the metals. When the metal content is low, one may only need a demetallization catalyst bed, in one reactor.

[0022] The nature of the reactions in the different reactors will be clear to the skilled artisan. To elaborate, hydrodemetalization, hydrodesulphurization, hydrodenitrogenation, hydrogenation, and cracking, all take place in the hydrotreater. Majority of cracking reactions take place in the reactors in the upgrading zone.

[0023] While not shown, the skilled artisan will understand that additional equipment, including exchangers, furnaces, pumps, columns, and compressors to feed the reactors, maintain proper operating conditions, and to separate reaction products, are all part of the systems described.

[0024] The catalysts used in the invention are those known to be used in the art for the stated purposes, especially those which contain one or more active metal components from Groups VI, VII, and/or VIII B of the Periodic Table plus alkali and alkaline metals and mixtures thereof. All catalysts are preferably incorporated, deposited, or in some way made part of a support, such as an alumina, alumina silica, silica, or zeolite support.

[0025] While the conditions under which the processes of the invention are carried out can vary, for the hydrotreating step, preferred conditions comprise a temperature of 300 - 500 °C, a pressure of from 1 - 200 Bar, LHSV of from 0.1 - 3.0 h⁻¹, and a hydrogen/oil ratio of 500 - 2500 L/L. More preferably, the temperature range is from 380 - 450 °C, the pressure ranges from 1 - 100 Bar, the LHSV ranges from 0.5 - 1.0 h⁻¹, and the hydrogen/oil ratio is preferably 1000 - 1500 L/L.

[0026] In the upgrading step, the preferred and especially preferred ranges are as above for hydrotreating. Preferred pressures are from 30 - 200 Bar, preferably 30 - 100 Bar. The LHSV is preferably 0.1 - 20.0 h⁻¹, and the hydrogen/oil ratio is as above for hydrotreating. The water/oil ratio may vary according to the skilled artisan.

[0027] Other embodiments will be clear to the skilled artisan and need not be reiterated here.

[0028] 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.

Claim:

1. A method for treating a hydrocarbon containing feedstock which has a boiling point greater than 300 °C, comprising:
 - (i) emulsifying said feedstock with an upgrading catalyst precursor, an aromatic rich hydrocarbon stream, and water to form an emulsion in the form of a slurry;
 - (ii) forming the catalyst by decomposing the said emulsion into a catalytic suspension, which is then transported to a hydrotreating reactor that contains a hydrotreating catalyst, said emulsion decomposition being carried out at a temperature of from about 300 °C to about 500 °C, and a pressure of from about 1 Bar to about 200 Bar;
 - (iii) fractionating said effluent into (a) contaminant gases, (b) a portion of light hydrocarbon gases having a boiling point of from 36 °C to 180 °C, (c) a portion of gas oil having a boiling point of from 180 °C to 375 °C, and (d) a portion of unconverted bottoms;
 - (iv) separating from (a) from (b), and (c) and transporting (b) and (c) to a recovery unit;
 - (v) combining said unconverted bottom with water, to form a slurry mixture;
 - (vi) transferring said slurry mixture to an upgrading reactor under conditions for cracking said mixture to form a light fraction containing (a), (b), (c), and (d) of step (ii);
 - (vii) transporting the unconverted bottoms from (vi) to a fractionation zone to remove light fractions therefrom, and
 - (viii) mixing any remaining unconverted bottoms with water in a feedstock preparation unit and subjecting said mixture to catalytic hydrothermal aquathermolysis.
2. The method of claim 1, further comprising adding hydrogen in step (vi).
3. The method of claim 1, wherein said temperature in step (ii) ranges from 380 °C to 450 °C.

4. The method of claim 1, wherein said pressure in step (i) ranges from 50 Bar to 180 Bar.
5. A method for treating a hydrocarbon containing feedstock which has a boiling point greater than 300 °C, comprising:
 - (i) combining said feedstock with hydrogen in a hydrotreating reactor which contains a hydrotreating catalyst, at a temperature of from about 300 °C to about 500 °C and a pressure from about 1 Bar to about 200 Bar, to form a first effluent containing (a) contaminant gases, (b) a portion of light hydrocarbon gases having a boiling point of from 36 °C to 180 °C, (c) a portion of gas oil having a boiling point of from 180 °C to 375 °C, and (d) a portion of unconverted bottoms;
 - (ii) transporting (a), (b), and (c) to a fractionation zone to separate (a), (b), and (c) from each other;
 - (iii) transporting said unconverted bottoms to a feedstock / catalyst preparation zone which contains an upgrading catalyst precursor, to form a mixture therebetween;
 - (iv) transporting said mixture to a decomposition zone;
 - (v) treating said mixture in (iv) to form said catalyst;
 - (vi) adding water to said mixture;
 - (vii) transporting said mixture to an upgrading reactor for reaction via catalytic hydrothermal aquathermolysis, to form a light fraction containing (a), (b), and (c) of step (i) and unconverted bottoms;
 - (viii) separating said light fraction and said unconverted bottoms;
 - (ix) transporting said light fraction to a fractionation zone to separate (a), (b), and (c) from each other, and
 - (x) recycling said unconverted bottoms to said upgrading reactor for further processing.
6. The method of claim 5, further comprising adding hydrogen in step (vi).

7. The method of claim 5, wherein the temperature in step (i) range from 380 °C to 450 °C.
8. The method of claim 5, wherein said pressure in step (i) ranges from 50 Bar to 180 Bar.
9. A method for treating a hydrocarbon containing feedstock which has a boiling point greater than 300 °C, comprising:
 - (i) simultaneously combining said feedstock with an upgrading catalyst precursor, wherein said catalyst precursor contains one or more of a Group VI, Group VII, Group VIIIB, alkali, or alkaline metal, on an alumina, alumina silica, silica, or zeolite support, water and hydrogen to form a mixture;
 - (ii) transporting said mixture to a decomposition reactor;
 - (iii) heating said mixture to form an upgrading catalyst;
 - (iv) transporting said mixture to an upgrading reactor;
 - (v) upgrading said mixture at a pressure of from 30-200 Bar, to form an effluent of (a) contaminant gases, (b) hydrocarbon gases having a boiling point of from 36 °C to 180 °C, (c) gas oil having a boiling point of from 180 °C to 375 °C, and (d) unconverted bottoms;
 - (vi) fractionating (a), (b), and (c) from said unconverted bottoms in a fractionation zone;
 - (vii) transporting said unconverted bottoms to a hydrotreating reactor which contains a hydrotreating catalyst, and hydrotreating said unconverted bottoms at a temperature of from about 300 °C to about 500 °C, an LHSV of from 0.1 to 20h⁻¹ and a pressure of from about 1 Bar to about 200 Bar, to form a fractionate of (a), (b), and (c) and unconverted bottoms;
 - (viii) transporting (a), (b), and (c) produced in step (v) and (vii) to a fractionation zone to separate (a), (b), and (c) from each other, and
 - (ix) recycling any unconverted bottoms from (vii) to said decomposition reactor for further processing.

10. The method of claim 9, wherein said temperature in step (vii) ranges from 380 °C to 450 °C.
11. The method of claim 9, wherein said pressure in step (vii) ranges from 50 Bar to 180 Bar.
12. The method of claim 9, wherein said hydrotreating reactor is a fixed bed, moving bed, slurry, plug flow, or CSTR.
13. The method of claim 9, wherein each reactor is a single or multiple reactors.
14. The method of claim 9, further comprising hydrotreating said unconverted bottoms at a pressure of from 50 Bar to 200 Bar.
15. The method of claim 9, wherein said pressure is from 30 to 100 Bar.
16. The method of claim 9, wherein said catalyst contains an alkali or alkaline metal.
17. The method of claim 16, wherein said catalyst is an alkali metal.
18. The method of claim 16, wherein said catalyst is an alkaline metal.