

HYDROPROCESSING IN MULTIPLE BEDS WITH INTERMEDIATE FLASH ZONES

This application is a continuation-in-part of co-pending application 10/001,737, filed October 25, 2001 and claims priority therefrom.

FIELD OF THE INVENTION

The invention relates to hydrocracking, and more particularly to hydrocracking occurring in more than one stage.

BACKGROUND OF THE INVENTION

In the refining of crude oil, vacuum gas oil hydrotreaters and hydrocrackers are employed to remove impurities such as sulfur, nitrogen and metals from the feed. Typically, the middle distillate boiling material (boiling in the range from 250°F - 735°F) from VGO hydrotreating or moderate severity hydrocrackers does not meet the smoke point, the cetane number or the aromatic specification required.

Removal of these impurities in subsequent hydroprocessing stages (often known as upgrading), creates more valuable middle distillate products. Hydroprocessing technology (which encompasses hydrotreating, hydrocracking and hydrodewaxing processes) aims to increase the value of the crude oil by fundamentally rearranging molecules. The end products are also made more environmentally friendly.

In most cases, this middle distillate is separately upgraded by a middle distillate hydrotreater or, alternatively, the middle distillate is blended into the general fuel oil pool or used as home heating oil. Recently hydroprocessing schemes have been developed which permit the middle distillate to be hydrotreated in the same high pressure loop as the vacuum gas oil hydrotreating reactor or the moderate severity hydrocracking reactor. The

1 investment cost saving and/or utilities saving are significant since a separate
2 middle distillate hydrotreater is not required.

3

4 There are several U.S. patent publications which are directed to multistage
5 hydroprocessing within a single high pressure hydrogen loop. In U.S. Patent
6 Application 20030111386, high conversion of heavy gas oils and the
7 production of high quality middle distillate products is possible in a single high-
8 pressure loop with reaction stages operating at different pressure and
9 conversion levels. The flexibility offered is great and allows the refiner to
10 avoid decrease in product quality while at the same time minimizing capital
11 cost. Feeds with varying boiling ranges are introduced at different sections of
12 the process, thereby minimizing the consumption of hydrogen and reducing
13 capital investment.

14

15 U.S. Patent Application 2003111387 also discloses multi-stage
16 hydroprocessing for the production of middle distillates. A major benefit of
17 this invention is the potential for simultaneously upgrading difficult cracked
18 stocks such as Light Cycle Oil, Light Coker Gas Oil and Visbroken Gas Oil or
19 Straight-Run Atmospheric Gas Oils utilizing the high-pressure environment
20 required for mild hydrocracking.

21

22 SUMMARY OF THE INVENTION

23

24 This invention, as are those discussed in the Background, is directed to
25 processes for upgrading the fraction boiling in the middle distillate range
26 which is obtained from VGO hydrotreaters and moderate severity
27 hydrocrackers. This invention preferably involves a multiple stage process
28 employing a single hydrogen loop. It could, however, be used in any fixed
29 bed hydroprocessing scheme such as mild hydrocracking, conventional single
30 stage or two stage hydrocracking and hydrotreating applications.

31

32 In this invention, removing distillate products as they are formed helps to
33 improve the environment of the cracking reactions by more effective utilization

1 of the reactor space, hydrogen and catalyst. Improved selectivity for
2 distillates results, providing the yield of low per pass conversion, but without
3 recycling large quantities of recycle oil.

4

5 The investment cost saving, as well as utilities savings, are significant since
6 the hydrocracking reactor could be potentially taken out of a conventional
7 recycle gas loop. Less catalyst volume and less hydrogen are required in the
8 hydrocracking reactor as well. This invention may be employed in a reactor
9 having multiple catalyst beds, or in a scheme employing several small, single
10 bed reactors in series. Improved catalyst kinetics and activity also result from
11 this invention.

12

13 The hydroprocessing method of the instant invention, which has at least two
14 reaction stages, comprises the following steps:

15

16 (a) passing a hydrocarbon feed into a first reaction stage which is
17 maintained at hydroprocessing conditions, where it is contacted
18 with a catalyst in at least one fixed bed and at least a portion of
19 the feed is converted;

20

21 (b) passing the effluent of step (a) to a hot high pressure separation
22 zone;

23

24 (c) separating the stream of step (b) into an unconverted liquid
25 effluent and a stream comprising converted products having
26 boiling points below that of the feed, said products being
27 subsequently passed to fractionation;

28

29 (d) passing the unconverted liquid effluent from step (c) to a second
30 reaction stage, said stage comprising a plurality of reaction
31 zones, wherein each zone is maintained at hydrocracking
32 conditions and separation occurs between each zone;

33

- 1 (e) contacting the feed in the first reaction zone of step (d) with a
2 catalyst in a fixed bed, thereby converting at least a portion of
3 the feed;
4
5 (f) separating the effluent of step (e) into an unconverted liquid
6 effluent, and a hydrogen-rich converted stream;
7
8 (g) passing the unconverted liquid effluent from step (f) to a second
9 reaction zone of the second stage, the zone being maintained at
10 hydrocracking conditions;
11
12 (h) contacting the feed in the second reaction zone of step (g) with
13 a catalyst in a fixed bed, thereby converting at least a portion of
14 the feed;
15
16 (i) fractionating the effluent of step (h) to produce one or more
17 middle distillate product streams.
18

19 BRIEF DESCRIPTION OF THE FIGURE

20
21 The Figure illustrates a schematic flow diagram of the instant invention. It is a
22 schematic of a two-stage hydrocracker. The second stage possesses at least
23 two reaction zones.
24

25 DETAILED DESCRIPTION OF THE INVENTION

26 Description Of The Preferred Embodiment

27
28
29 The Figure illustrates the preferred embodiment of the invention. The oil feed
30 in line 1 is preheated, and pumped up to the first stage hydrotreating reactor
31 pressure by the first stage feed pump (not shown). Oil feed in line 1 is
32 combined with preheated recycle gas (line 2) to form line 3. Line 3 is further
33 heated by process heat exchange (not shown). Line 3 is also heated in the

1 first stage feed furnace 5.

2

3 The combined feed is sent to the first stage hydrotreating reactor 10. In this
4 reactor, the feed is hydrotreated and partially hydrocracked. Hydrogen
5 recycle gas (line 4) is used to quench the reaction exothermic heat release.
6 The effluent from this reactor, line 6, is composed of H_2S , NH_3 , light gases,
7 naphtha, middle distillate and hydrotreated heavy gas oil.

8

9 This first stage reactor effluent 6 is then cooled by preheating feed and/or
10 steam generation (exchanger bank 25) and routed to a Hot High Pressure
11 Separator (HHPS) 30 situated between the first stage hydrotreating reactor
12 and the second stage hydrocracking reactor. In HHPS, most of the 700-
13 material is removed through line 8 and sent to hydrogen recovery and product
14 fractionation. Material in line 8 is cooled (by steam generation or process
15 heat exchange) and sent to a Cold High Pressure Separator (not shown) on
16 its way to the recycle gas compressor.

17

18 HHPS is operated at a slightly lower pressure than the first stage
19 hydrotreating reactor. HHPS bottoms, line 7, mainly composed of
20 unconverted oil, is let-down under pressure (valve 35), combined with line 12,
21 mixed with fresh makeup hydrogen (line 13) and routed to the inlet of the
22 second stage hydrotreating or hydrocracking reactor 20. Line 12 is composed
23 of recycle oil from fractionation (line 9) and fresh aromatic feed oil (line 11).

24

25 The liquid from the top bed (20a) of this hydrotreating or hydrocracking
26 reactor is taken out (line 16) and flashed in a side vessel 40. Distillate
27 products are removed overhead via line 17. The liquid from this side vessel
28 40 is removed via line 18 and is cooled in an indirect heat exchanger 45
29 heating a process stream and put back to the bed below (20b) after added
30 adequate fresh makeup hydrogen (line 23). This set is repeated for the
31 subsequent beds in the hydrocracking reactor, with the effluent of bed 20b
32 (line 19) being taken out and flashed in a side vessel 50. Distillate products
33 are removed overhead via line 21. The liquid from this side vessel 50 is

1 removed via line 22 and is cooled in an indirect heat exchanger 55 heating a
2 process stream and put back to the bed below (20c) under its own pressure
3 by gravity flow after added adequate fresh makeup hydrogen (line 26). The
4 final liquid product is removed via line 23.

5

6 The total fresh makeup hydrogen for the plant is routed through the second
7 stage hydrocracking reactor and the excess hydrogen arrives back in the
8 recycle gas loop at the recycle gas compressor suction to satisfy the needs of
9 first stage reactor.

10

11 The concept of removing products as they are formed results in better
12 utilization of the given second stage hydrocracking reactor catalyst volume by
13 incrementally increasing the true residence time available for the still
14 unconverted oil and by delivering shots of high purity hydrogen to where
15 specifically needed in the liquid phase. This further gives an incremental
16 kinetics boost and results in higher per pass conversion. This gives the direct
17 benefit of less recycle liquid from fractionator bottoms to achieve desired
18 target conversion.

19

20 A customized hydrocracking catalyst system in an ascending/descending
21 temperature profile would be used in the second stage reactor using relatively
22 mild hydrocracking catalyst at the top beds and progressively higher activity
23 stable (zeolitic) hydrocracking catalysts in subsequent beds.

24

25 Converted material from the Cold High Pressure Separator, side vessels, and
26 reactor effluents from subsequent stages could be combined or kept separate
27 and sent to product distillation and recovery. Or the second stage effluent
28 could be post-treated by adding catalyst in the side vessels or in a
29 downstream, low pressure, cleaner environment post-treat step.

30

31 The product distillation (not shown) could be a combined unit operation for the
32 first stage hydrotreating reactor and second stage hydrocracking reactor
33 products or could be a divided unit operation (within one shell) for separate

1 distillation of first stage hydrotreating reactor and second stage hydrocracking
2 reactor products.

3

4 In either step, the HHPS bottoms liquid would be cooled only to around 650F
5 (or desired second stage hydrocracking reactor inlet temperature) and using a
6 hot high differential pressure pump directly sent to the second stage inlet
7 without the need for an intermediate cooling/heating train or storage or a
8 furnace. If required, any startup heating requirement of the second stage
9 hydrocracking reactor could be combined with the first stage hydrotreating
10 reactor feed furnace.

11

12 **Feeds**

13

14 A wide variety of hydrocarbon feeds may be used in the instant invention.
15 Typical feedstocks include any heavy or synthetic oil fraction or process
16 stream having a boiling point above 392F (200C). Feeds to this invention
17 generally include hydrocarbons boiling in the range from 500F to 1500F.
18 Such feedstocks include vacuum gas oils, demetallized oils, deasphalted oil,
19 Fischer-Tropsch streams, FCC and coker distillate streams, heavy crude
20 fractions, etc. Other streams include heavy atmospheric gas oil, delayed
21 coker gas oils, visbreaker gas oils, aromatic extracts, heavy residue thermal
22 or catalyst upgrader gas oils, and thermal or catalyst fluid cracker cycle oils.
23 Typical feedstocks contain from 100-5000 ppm nitrogen and from 0.2-5 wt. %
24 sulfur.

25

26 The recycle oil (from the product distillation) can be introduced at the second
27 stage hydrocracking inlet or at a suitable bed.

28

29 **Products**

30

31 The hydrocracking process of this invention is especially useful in the
32 production of middle distillate fractions boiling in the range of about 250 -
33 700F (121 - 371C). A middle distillate fraction is defined as having a boiling

1 range from about 250 to 700F. The term "middle distillate" includes the
2 diesel, jet fuel and kerosene boiling range fractions. The kerosene or jet fuel
3 boiling point range refers to the range between 280 and 525F (138-274C).
4 The term "diesel boiling range" refers to hydrocarbons boiling in the range
5 from 250 to 700F (121 - 371C). Gasoline or naphtha normally boils in the
6 range below 400 (204C). Boiling ranges of various product fractions
7 recovered in any particular refinery will vary with such factors as the
8 characteristics of the crude oil source, local refinery markets and product
9 prices.

10

11 **Conditions**

12

13 [0032] Hydroprocessing conditions is a general term which refers primarily in
14 this application to hydrocracking or hydrotreating, preferably hydrocracking.

15

16 [0033] Hydrotreating conditions include a reaction temperature between 400F
17 - 900F (204C - 482C), preferably 650F - 850F (343C - 454C); a pressure
18 between 500 to 5000 psig (pounds per square inch gauge) (3.5-34.6 MPa),
19 preferably 1000 to 3000 psig (7.0-20.8 MPa); a feed rate (LHSV) of 0.5 hr (-1)
20 to 20 hr (-1) (v/v); and overall hydrogen consumption 300 to 2000 scf per
21 barrel of liquid hydrocarbon feed (53.4-356 m³/m³ feed).

22

23 [0034] Typical hydrocracking conditions include a reaction temperature of
24 from 400F - 950F (204C - 510C), preferably 650F - 850F (343C - 454C).
25 Reaction pressure ranges from 500 to 5000 psig (3.5-34.5 MPa), preferably
26 1500-3500 psig (10.4-24.2 MPa). LHSV ranges from 0.1 to 15 hr (-1)(v/v),
27 preferably 0.25-2.5 hr (-1). Hydrogen consumption ranges from 500 to 2500
28 scf per barrel of liquid hydrocarbon feed (89.1445m³H₂/m³ feed).

29

30 **Catalyst**

31

32 A hydroprocessing zone may contain only one catalyst, or several catalysts in
33 combination.

1

2 The hydrocracking catalyst generally comprises a cracking component, a
3 hydrogenation component and a binder. Such catalysts are well known in the
4 art. The cracking component may include an amorphous silica/alumina phase
5 and/or a zeolite, such as a Y-type or USY zeolite. Catalysts having high
6 cracking activity often employ REX, REY and USY zeolites. The binder is
7 generally silica or alumina. The hydrogenation component will be a Group VI,
8 Group VII, or Group VIII metal or oxides or sulfides thereof, preferably one or
9 more of molybdenum, tungsten, cobalt, or nickel, or the sulfides or oxides
10 thereof. If present in the catalyst, these hydrogenation components generally
11 make up from about 5% to about 40% by weight of the catalyst. Alternatively,
12 noble metals(preferably used in lower beds), especially platinum and/or
13 palladium, may be present as the hydrogenation component, either alone or in
14 combination with the base metal hydrogenation components molybdenum,
15 tungsten, cobalt, or nickel. If present, the platinum group metals will generally
16 make up from about 0.1% to about 2% by weight of the catalyst.

17

18 Hydrotreating catalyst is preferably used in the upper beds. Hydrotreating
19 catalysts will typically be a composite of a Group VI metal or compound
20 thereof, and a Group VIII metal or compound thereof supported on a porous
21 refractory base such as alumina. Examples of hydrotreating catalysts are
22 alumina supported cobalt-molybdenum, nickel sulfide, nickel-tungsten, cobalt-
23 tungsten and nickel-molybdenum. Typically, such hydrotreating catalysts are
24 presulfided.

1 What is claimed is:

2

3 1. The hydroprocessing method of the instant invention, which has at
4 least two reaction stages, comprises the following steps:

5

6 (a) passing a hydrocarbon feed into a first reaction stage which is
7 maintained at hydroprocessing conditions, where it is contacted
8 with a catalyst in at least one fixed bed and at least a portion of
9 the feed is converted;

10

11 (b) passing the effluent of step (a) to a hot high pressure separation
12 zone;

13

14 (c) separating the stream of step (b) into an unconverted liquid
15 effluent and a stream comprising converted products having
16 boiling points below that of the feed, said products being
17 subsequently passed to fractionation;

18

19 (d) passing the unconverted liquid effluent from step (c) to a second
20 reaction stage, said stage comprising a plurality of reaction
21 zones, wherein each zone is maintained at hydrocracking
22 conditions and separation occurs between each zone;

23

24 (e) contacting the feed in the first reaction zone of step (d) with a
25 catalyst in a fixed bed, thereby converting at least a portion of
26 the feed;

27

28 (f) separating the effluent of step (e) into an unconverted liquid
29 effluent, and a hydrogen-rich converted stream;

30

31 (g) passing the unconverted liquid effluent from step (f) to a second
32 reaction zone of the second stage, the zone being maintained at
33 hydrocracking conditions;

1

2 (h) contacting the feed in the second reaction zone of step (g) with
3 a catalyst in a fixed bed, thereby converting at least a portion of
4 the feed;

5

6 (i) fractionating the effluent of step (h) to produce one or more
7 middle distillate product streams.

8

9 2. The process of claim 1, wherein fresh feed may be combined with the
10 unconverted liquid effluent of step (c) before entering the second
11 reactor stage.

12

13 3. The process of claim 1, wherein the second reaction stage may
14 comprise a reactor having multiple catalyst beds.

15

16 4. The process of claim 1, wherein the second reaction stage may
17 comprise several small, single bed reactors in series.

18

19 5. The process of claim 1, wherein the inlet temperature of each reaction
20 zone in the second stage subsequent to the first reaction zone is lower
21 than the previous one and the outlet temperature of each reaction zone
22 subsequent to the first reaction zone is lower than the previous one.

23

24 6. The process of claim 5, wherein the average reaction temperature of
25 each reaction zone subsequent to the first reaction zone is at least 50F
26 lower than the average reaction temperature of the previous one.

27

28 7. The process of claim 1, wherein the catalyst of each reaction zone of
29 the second stage is a hydrocracking catalyst.

30

31 8. The process of claim 7, in which the catalyst in each bed subsequent
32 to the first one in the second stage reaction zone demonstrates
33 increasing activity.

- 1 9. The process of claim 7, wherein each of the reaction zones of the
2 second stage is operated under hydrocracking conditions including
3 temperatures in the range from about 400 - 950F (204 - 510C),
4 reaction pressure in the range from 500 through 5000 psig (3.5-34.5
5 MPa), LHSV of 0.1 to 15 hr (-1), and hydrogen consumption of 500
6 through 2500 scf per barrel of liquid hydrocarbon feed (89.1-445 m³ H₂
7 feed).
8
- 9 10. The process of claim 9, wherein more preferred hydrocracking
10 conditions include a temperature range from 650 - 850F (343 C.-454
11 C), reaction pressure from 1500 psig through 3500 psig (10.4-24.2
12 MPa) and LHSV 0.25 through 2.5 hr (-1), and hydrogen consumption of
13 500 through 2500 scf per barrel of liquid hydrocarbon feed (89.1-445
14 m³ H₂ feed).
15
- 16 11. The process of claim 1, wherein the unconverted effluent comprises
17 hydrocarbons which boil above 700F.
18
- 19 12. The process of claim 1, wherein the converted stream comprises
20 hydrocarbons boiling below 700F.
21
- 22 13. The process of claim 1, wherein one or more side vessels comprises
23 hydroprocessing catalyst for further upgrading.
24
- 25 14. The process of claim 12, wherein the converted stream from each
26 reaction zone may be fractionated separately or be combined, then
27 fractionated into at least one fuel product.
28
- 29 15. The process of claim 1, wherein at least two of the reaction stages
30 operate within a single high-pressure hydrogen loop.
31
- 32 16. The process of claim 15, wherein the reaction stages operate at
33 different pressure and conversion levels.

1

2 17. The process of claim 14, wherein the preferred fuel product is diesel.

3

4 18. The process of claim 14, wherein the preferred fuel product is jet fuel.

5

6 19. The process of claim 14, wherein the preferred fuel product is naphtha.

7

8 20. The process of claim 1, wherein the feed is subjected to a preliminary
9 hydrotreating step.