

1 **HIGH CONVERSION HYDROPROCESSING**
2 **USING MULTIPLE PRESSURE AND REACTION ZONES**

3
4 FIELD OF THE INVENTION

5
6 This invention is directed to hydroprocessing, and more particularly to
7 multistage hydroprocessing.

8
9 BACKGROUND OF THE INVENTION

10
11 This process is directed to hydroprocessing, preferably by hydrocracking heavy
12 hydrocarbon material boiling in the vacuum gas oil range to produce middle
13 distillates at very high selectivity, and to upgrade lower-value distillates by
14 hydrotreating. The concept includes many innovations which would allow the
15 refiner to obtain yields similar to those of a multistage hydrocracker with the
16 economics of a single stage, once-through unit.

17
18 Previous designs for hydroprocessing vacuum gas oils or other hydrocarbon
19 materials boiling in a range of 392°F or greater include:

- 20
- 21 • Straight forward single stage once through design. Conversion ranges
22 from 20% to 80%. The amount of bottoms produced is greater than or
23 equal to 20%.
 - 24
 - 25 • Single stage recycles. Conversion ranges from 90% to 99%
26 conversion. The amount of bottoms produced is less than or equal to
27 10%. Recycle liquid operation can result in complications, however.
 - 28
 - 29 • Multistage recycle results in higher cost than single stage once through
30 or single stage recycle. It does provide, however, the highest liquid
31 yield and most flexibility. Conversion is from 95% to 100%. Bottoms
32 produced are less than 5%.

- Split-feed injection in cases where external distillate feeds are employed.

None of these processes can readily upgrade external feeds (raw feeds from outside the hydroprocessing unit), unless they go through captive process loop.

SUMMARY OF THE INVENTION

The disclosed method is designed to obtain yields similar to those obtained with multistage recycle but at a much lower capital investment. It is intended to simultaneously upgrade external, low-value distillates while hydrocracking feeds boiling in the vacuum gas oil range.

The configuration may involve a once-through liquid hydroprocessing unit having at least two reactors. One is preferably for hydrotreating, and one is preferably for hydrocracking in a clean environment at lower pressure. Between the first and second reactors may be a very hot high pressure separator which flashes first reactor product distillate overhead to a distillate upgrader.

Advantages of the disclosed method include:

- (1) Lower capital cost than found in earlier designs because of:
 - (a) lower pressure in hydrocracking reactor and distillates upgrader;
 - (b) a clean environment for hydrocracking in subsequent reactors;
 - (c) a smaller overall catalyst volume is required; and
 - (d) amount of major equipment (pumps, furnaces, compressors, etc.) is minimized.

1 (2) Higher conversion results, relative to a typical single stage once
2 through hydroprocessing unit. Subsequent reactors operate in a clean
3 environment and can accomplish high conversions at much lower
4 temperatures than the bottoms beds of a single stage once through
5 hydroprocessing unit.

6
7 (3) Overcracking of distillates is minimized due to the very hot high
8 pressure separator following the first reactor. In this separator the bulk
9 of the distillates are removed overhead and thus are prevented from
10 reaching the hydrocracking reactor. This innovation leads to high
11 distillate selectivity (distillate yield/conversion). The distillate selectivity
12 approaches the 95% achievable in a recycle unit having two or more
13 stages.

14
15 (4) Split feed injection with segregated reaction zones. Upgrading of
16 external distillates occurs at the same time as vacuum gas oil
17 hydrocracking without separate fractionation zones. This concept
18 differs from earlier split feed designs in the lower operating pressure
19 employed at the point of split feed injection. Furthermore, the feed is
20 injected at different points than those used in previous inventions.

21
22 (5) Lower consumption of H_2 and lower catalyst volume because the
23 reaction zones are optimized for their functions. (HDT of VGO at high
24 pressure, recovery/upgrading of distillates, HCR of VGO bottoms
25 provides a clean environment).

26
27 The development of the disclosed method has been promoted by the
28 following observations:

29
30 (1) Hydrotreating of material boiling in the vacuum gas oil range is much
31 more effective at higher hydrogen pressure than lower hydrogen
32 pressure.

1 (2) Hydrocracking of bottoms from a hydrotreated vacuum gas oil feed can
2 occur at 50°F to 100°F lower temperature in a clean environment than in
3 the bottoms beds of a single stage once through process.
4

5 (3) Diesel overlap will crack when mixed in with vacuum gas oil in a
6 hydrocracker.
7

8 (4) A noble metal zeolite hydrocracking catalyst will function very well in
9 the second reactor or subsequent reactor. A base metal zeolite
10 hydrocracking catalyst can also be used.
11

12 (5) Calculations indicate this process configuration can accomplish >90%
13 conversion with 94% to 96% selectivity to 250°F to 700°F distillates
14 produced from a straight run vacuum gas oil.
15

16
17 In one aspect, there is provided an integrated hydroprocessing method
18 having at least two stages, each stage
19 further comprising at least one reaction zone, said method comprising the
20 following steps:
21

22 (a) combining an oil feed with a hydrogen-rich gas stream to form a
23 feedstock;
24

25 (b) passing the feedstock of step (a) to a reaction zone of the
26 first stage, which is maintained at conditions sufficient to effect a
27 boiling range conversion, and contacting it with hydroprocessing
28 catalyst, thereby creating a hydroprocessed effluent;
29

30 (c) passing the effluent of step (b), following pressure reduction, to
31 a very hot separator maintained at high pressure, where it is
32 separated into an overhead fraction and a bottoms fraction;

- 1 (d) passing the overhead fraction of step (c) to a distillate upgrader
2 which contains at least one zone of hydroprocessing catalyst
3 and is maintained at conditions sufficient to effect a boiling
4 range conversion, thereby creating an upgraded effluent;
5
- 6 (e) passing the bottoms fraction of step (c) to a reaction zone of the
7 second stage, which is maintained at conditions sufficient to
8 effect a boiling range conversion, and contacting it with
9 hydroprocessing catalyst thereby creating a second
10 hydroprocessed effluent;
11
- 12 (f) combining the upgraded effluent of step (d) with the second
13 hydroprocessed effluent of step (e) , the combined stream then
14 entering a hot separator maintained at high pressure, in which
15 the combined stream is separated into an overhead fraction and
16 a bottoms fraction, the bottoms fraction proceeding to
17 fractionation;
18
- 19 (g) passing the overhead fraction of step (f) to a cold separator,
20 where it is separated into an overhead fraction comprising
21 hydrogen and light gases, and a bottoms fraction comprising
22 sour water.
23

24 BRIEF DESCRIPTION OF THE FIGURES

- 25
- 26 Figure 1 illustrates the multistage recycle process of the instant invention.
27
- 28 Figures 2 and 3 shows a comparison of conventional and new hydrocracking
29 configurations using a base metal catalyst system. Figure 2 illustrates catalyst
30 temperature vs. conversion and Figure 3 compares middle distillate
31 yield vs. conversion.

DETAILED DESCRIPTION OF THE INVENTION

Description of the Preferred Embodiment

Figure 1 illustrates feed entering the process through stream 1 and being combined with hydrogen in stream 28 to form stream 2. Hydrogen in stream 28 is prepared by compression of hydrogen in makeup compressor 85. Hydrogen enters compressor 85 through stream 27. The invention includes an option to compress a stream 30 of recycle gas in the last stage of compressor 85 to meet the gas to oil ratio in reactor 10, when required.

Stream 2 is heated, as depicted by exchanger 31, prior to entering the first stage hydroprocessing unit, vessel 10. Vessel 10 is preferably operated as a hydrotreater. The feed flows downward through one or more beds of catalyst. Streams 3, 4, and 5 depict interbed hydrogen quench.

Hydrotreated effluent exits vessel 10 through stream 32 and is reduced in pressure (valve 33) to that required for hydrocracking in a clean environment. The effluent is heated in furnace 34 to approximately 825°F in order to disengage the maximum material in very hot high pressure separator 20. This separator functions as a simple flash drum, separating diesel and lighter fractions from heavier materials without the use of hydrogen stripping. Hydrogen stripping is relatively ineffective at hydrocracking pressures. Stream 11, containing diesel and lighter materials, exits vessel 20 overhead. External feeds in the middle distillate boiling range, as well as fractionation recycle, are represented by stream 9 and are combined with stream 11. Stream 11 is heated in exchanger 35 and may be combined with hydrogen in stream 25 prior to entering a distillate upgrader, vessel 30, in the case of co-current flow. Flow in vessel 30 may be co-current or countercurrent. Countercurrent flow may be preferred if aromatics saturation is desired. The amount of aromatics permitted in the ultra-low sulfur diesel being manufactured (ULSD) may affect whether co-current or counter-current flow is

1 used. In the case of countercurrent flow, hydrogen is added below the catalyst
2 beds and is directed upward. The catalyst in the bed or beds of vessel 30 is
3 preferably hydrotreating catalyst, but hydrocracking catalyst may be used if
4 fractionation recycle is being treated.

5
6 The bottoms effluent of vessel 30 exits through stream15. Material from
7 stream15 may be passed to stream12 as feed to the hydrocracker, vessel 40,
8 when necessary. The dotted line depicts this. The upgraded diesel effluent in
9 stream15 is reduced in pressure (valve 36), cooled (exchanger 37), combined
10 with the effluent stream (stream14) from vessel 40 (in which second stage
11 hydrocracking preferably occurs) to become stream16. Stream16 is passed to
12 the hot high pressure separator 70, where it is separated into an overhead
13 stream 18 and a bottoms stream 17. Bottoms stream 17 is sent to
14 fractionation. Overhead stream 18 is cooled prior to entering cold high
15 pressure separator 50 by passage through exchangers 43 and 44, as well as
16 by water injection through stream 19. Sour water exits cold high pressure
17 separator through stream 29. Stream 71 goes to fractionation. It may be
18 reduced in pressure using valve 72. Overhead gaseous material in stream 21
19 enters amine absorber, vessel 60 at the bottom and flows upward, as lean
20 amine moves downward, absorbing hydrogen sulfide. Rich amine exits vessel
21 60 through stream 22. Stream 23, comprising primarily hydrogen, exits
22 overhead through stream 23. Stream 23 is compressed in compressor 75,
23 becoming stream 24. Stream 24 is divided into streams 25 and 26. Stream 26
24 is heated in exchanger 42 before combining with stream 12 to form stream 13.

25

26 The bottoms effluent of vessel 20 exits through stream12. Valve 38 is a level
27 control valve. Stream12 may be combined with material in stream 15, along
28 with hydrogen in stream 26 then is heated in exchanger 39. Streams 12 and
29 15 may be combined when naphtha or jet fuel is the preferred product.
30 Recycle stream 31 may be added to stream 15 when very high conversion
31 levels are required. Stream 13 exits exchanger 39 and enters vessel 40.
32 Second stage hydrocracking preferably occurs in vessel 40, which contains

one or more beds of hydrocracking catalyst. Effluent in stream 14 is cooled in exchanger 41 before being combined with stream 16.

Feeds

A wide variety of hydrocarbon feeds may be used in the instant invention. Typical feedstocks include any heavy or synthetic oil fraction or process stream having a boiling point above 392°F (200°C). Such feedstocks include vacuum gas oils (VGO), heavy coker gas oil (HCGO), heavy atmospheric gas oil (AGO), light coker gas oil (LCGO), visbreaker gas oil (VBGO), demetallized oils (DMO), vacuum residua, atmospheric residua, deasphalted oil, Fischer-Tropsch streams, Light Cycle Oil and other FCC product streams.

Products

The process can be used over a broad range of applications as shown in the Table 1.

TABLE 1

Oil Feed	Catalyst System	Operating Conditions	Products
VGO HCGO DAO VBGO	Stage 1- Hydrotreating + Hydrocracking Stage 2- Hydrocracking	Stage 1: P: 1000 - 3000 psig LHSV = 0.3 - 4.0 T: 600°F - 850°F Stage 2: P: 1000 - 3000 psig LHSV = 0.5 - 5.0 T: 500°F - 800°F	• Maximum Diesel • Maximum Jet+Diesel • Maximum Naphtha
AGO, LCO, LCGO	Stage 1- Hydrotreating+Hydrocracking Stage 2- Hydrocracking or Stage 2- Base Metal Hydrocracking or Stage 2- Aromatic Saturation (Noble-metal)	Stage 1: P: 1000 - 3000 psig LHSV=0.5 - 4.0 T: 600°F - 850°F Stage 2: P: 1000 - 3000 psig LHSV = 0.5 - 5.0 T: 500°F - 750°F	• Maximum Diesel • Maximum Jet+Diesel • Maximum Naphtha

The process of this invention is especially useful in the production of middle distillate fractions boiling in the range of about 250°F to 700°F (121°C to 371°C). A middle distillate fraction is defined as having an

1 approximate boiling range from about 250°F to 700°F. At least 75 vol.%,
2 preferably 85 vol.% of the components of the middle distillate has a normal
3 boiling point of greater than 250°F. At least about 75 vol.%, preferably
4 85 vol.% of the components of the middle distillate has a normal boiling point
5 of less than 700°F. The term "middle distillate" includes the diesel, jet fuel and
6 kerosene boiling range fractions. The kerosene or jet fuel boiling point range
7 refers to the range between 280°F and 525°F (38°C to 274°C). The term
8 "diesel boiling range" refers to hydrocarbons boiling in the range from
9 250°F to 700°F (121°C to 371°C).

10

11 Gas streams or naphtha may also be produced in the process of this
12 invention. Gas streams or naphtha normally boils in the range below 400°F
13 (204°C), or from C₅ to 400°F (204°C). Boiling ranges of various product
14 fractions recovered in any particular refinery will vary with such factors as the
15 characteristics of the crude oil source, local refinery markets and product
16 prices.

17

18 **Conditions**

19

20 A hydroprocessing condition is a general term which refers primarily in this
21 application to hydrocracking or hydrotreating.

22

23 Hydrotreating conditions include a reaction temperature between
24 400°F to 900°F (204°C to 482°C), preferably 650°F to 850°F
25 (343°C to 464°C); a pressure between 500 to 5000 psig (pounds per square
26 inch gauge) (3.5 to 34.6 MPa), preferably 1000 to 3000 psig
27 (7.0 to 20.8 MPa); a feed rate (LHSV) of 0.5 to 20 hr⁻¹ (v/v); and overall
28 hydrogen consumption 300 to 2000 SCF per barrel of liquid hydrocarbon feed
29 (63.4 to 356 m³/m³ feed. The second stage hydrotreating reactor is operating
30 at a lower pressure than the first stage reactor, the VGO hydrotreater or
31 moderate severity hydrocracker.

1 Typical hydrocracking conditions (which may be found in stage 1 or stage 2)
2 include a reaction temperature of from 400°F to 950°F (204°C to 510°C)
3 preferably 650°F to 850°F (343°C to 454°C). Reaction pressure ranges from
4 500 to 5000 psig (3.5 to 4.5 MPa), preferably 1500 to 3500 psig
5 (10.4 to 24.2 MPa). LHSV ranges from 0.1 to 15 hr⁻¹ (v/v), preferably
6 0.25 to 2.5 hr⁻¹ hydrogen consumption ranges from 500 to 2500 SCF per barrel
7 of liquid hydrocarbon feed (89.1 to 445 m³H₂/m³ feed).

8

9 Catalyst

10

11 A hydroprocessing zone may contain only one catalyst, or several catalysts in
12 combination.

13

14 The hydrocracking catalyst generally comprises a cracking component, a
15 hydrogenation component and a binder. Such catalysts are well known in the
16 art. The cracking component may include an amorphous silica/alumina phase
17 and/or a zeolite, such as a Y-type or USY zeolite. Catalysts having high
18 cracking activity often employ REX, REY and USY zeolites. The binder is
19 generally silica or alumina. The hydrogenation component will be a Group VI,
20 Group VII, or Group VIII metal or oxides or sulfides thereof, preferably one or
21 more of molybdenum, tungsten, cobalt, or nickel, or the sulfides or oxides
22 thereof. If present in the catalyst, these hydrogenation components generally
23 make up from about 5% to about 40% by weight of the catalyst. Alternatively,
24 platinum group metals, especially platinum and/or palladium, may be present
25 as the hydrogenation component, either alone or in combination with the base
26 metal hydrogenation components molybdenum, tungsten, cobalt, or nickel. If
27 present, the platinum group metals will generally make up from about
28 0.1% to about 2% by weight of the catalyst.

29

30 If aromatic saturation is particularly desired, a preferred catalyst has a
31 crystalline molecular sieve material component and a Group VIII noble metal
32 component. The crystalline molecular sieve material component is a large
33 pore faujasite structure having an alpha acidity of less than 1, preferably less

1 than 0.3. Zeolite USY is the preferred crystalline molecular sieve material
2 component.
3
4 Hydrotreating catalyst, if used, will typically be a composite of a Group VI
5 metal or compound thereof, and a Group VIII metal or compound thereof
6 supported on a porous refractory base such as alumina. Examples of
7 hydrotreating catalysts are alumina supported cobalt-molybdenum, nickel
8 sulfide, nickel-tungsten, cobalt-tungsten and nickel-molybdenum. Typically,
9 such hydrotreating catalysts are presulfided.

11 EXAMPLES

13 TABLE 2

14 **Comparison of Standard and New HCR Configurations**
15 Middle East VGO, Base Metal Catalyst System 73 vol.% Conversion <700°F
16

	Conventional	New
LHSV, 1/br	0.75	0.75
Catalyst Temperature, °F	777	727*
HCR Zone Pressure, psig	2300	1250
Chemical H ₂ Consumption, SCF/3	1800	1600
Middle Distillate Yield, liquid volume% 250°F to 700°F	67	68

17 *706°F at equal gas/oil ratio for standard and new configurations
18

19 Table 2 indicates that yield is slightly improved in the current invention, as
20 compared to the conventional configuration, at lower temperature, pressure
21 and hydrogen consumption.

22
23 Figure 2 demonstrates that conversion in the instant invention is greater at
24 lower temperatures, as opposed to the conventional hydrocracking
25 configuration. Conversion improves at higher gas to oil ratios.

26
27 Figure 3 demonstrates that yield to conversion ratios are comparable in both
28 the conventional configuration as well as the configuration of the instant
29 invention.

1 WHAT IS CLAIMED IS:

2

3 1. An integrated hydroprocessing method having at least two stages,
4 each stage further comprising at least one reaction zone which
5 comprises hydroprocessing catalyst, said method comprising the
6 following steps:

7

8 (a) combining an oil feed with a hydrogen-rich gas stream to form a
9 feedstock;

10

11 (b) passing the feedstock of step (a) to a reaction zone of the first
12 stage, which is maintained at conditions sufficient to effect a
13 boiling range conversion, and contacting it with hydroprocessing
14 catalyst, thereby creating a hydroprocessed effluent;

15

16 (c) passing the effluent of step (b) to a very hot separator
17 maintained at high pressure, where it is separated into an
18 overhead fraction and a bottoms fraction;

19

20 (d) passing the overhead fraction of step (c) to a distillate upgrader
21 which contains at least one zone of hydroprocessing catalyst
22 and is maintained at conditions sufficient to effect a boiling
23 range conversion, thereby creating an upgraded effluent;

24

25 (e) passing the bottoms fraction of step (c) to a reaction zone of the
26 second stage, which is maintained at conditions sufficient to
27 effect a boiling range conversion, and contacting it with
28 hydroprocessing catalyst thereby creating a second
29 hydroprocessed effluent;

30

31 (f) combining the upgraded effluent of step (d) with the second
32 hydroprocessed effluent of step (e), the combined stream then
33 entering a hot separator maintained at high pressure, in which

1 the combined stream is separated into an overhead fraction and
2 a bottoms fraction, the bottoms fraction proceeding to
3 fractionation;

4

5 (g) passing the overhead fraction of step (f) to a cold separator
6 maintained at high pressure, where it is separated into an
7 overhead fraction comprising hydrogen and light gases, and a
8 bottoms fraction comprising sour water.

9

10 2. The method of claim 1, wherein the overhead fraction of step (g) is
11 passed through an amine absorber prior to passing to a recycle gas
12 compressor.

13

14 3. The method of claim 1, in which material to be upgraded and hydrogen
15 may flow co-currently or countercurrently to each other in the distillate
16 upgrader of step (d).

17

18 4. The method of claim 1, in which the first stage reaction zone comprises
19 at least one bed of catalyst selected from the group consisting of
20 hydrotreating catalyst, hydrocracking catalyst or a combination of both,
21 either alone or in combination with each other, and the second stage
22 reaction zone comprises at least one bed of hydrocracking catalyst.

23

24 5. The method of claim 4, wherein the hydrocracking catalyst of the
25 second stage comprises a base metal, base metal combination, a
26 noble metal or a noble metal combination.

27

28 6. The method of claim 1, in which at least a portion of the upgraded
29 effluent of step (d) is combined with the bottoms fraction of step (c) and
30 passed to the reaction zone of the second stage;

31

32 7. The method of claim 3, in which the distillate upgrader comprises
33 aromatic saturation catalyst when counter-current flow is occurring.

- 1 8. The method of claim 7, in which the aromatic saturation catalyst
2 comprises a noble metal or combination of noble metals.
3
- 4 9. The method of claim 1, in which the feedstocks possess a boiling point
5 of at least 392°F.
6
- 7 10. The method of claim 9, wherein the oil feed is selected from the group
8 consisting of vacuum gas oils (VGO), heavy coker gas oil (HCGO),
9 heavy atmospheric gas oil (AGO), light coker gas oil, visbreaker gas oil
10 (VBGO), demetallized oils (DMO), vacuum residua, atmospheric
11 residua, deasphalted oil, Fischer-Tropsch streams, Light Cycle Oil,
12 Light Cycle Gas Oil and FCC streams.
13
- 14 11. The method of claim 1, in which the products comprise middle distillate
15 fractions boiling in the range of from 250°F to 700°F.
16
- 17 12. The method of claim 11, in which the products comprise naphtha,
18 jet fuel, diesel and kerosene.
19
- 20 13. The method of claim 1, in which interbed hydrogen quench is used in
21 stage one.
22
- 23 14. The method of claim 1, in which hydrotreating conditions comprise a
24 reaction temperature between 400°F to 900°F, a pressure between
25 500 to 5000 psig, a feed rate (LHSV) of 0.5 to 20 hr⁻¹ (v/v); and overall
26 hydrogen consumption 300 to 2000 SCF per barrel of liquid
27 hydrocarbon feed (63.4 to 356 m³/m³ feed).
28
- 29 15. The method of claim 1, in which hydrocracking conditions comprise a
30 reaction temperature of from 400°F to 950°F, reaction pressure ranges
31 from 500 to 5000 psig, and LHSV ranges from 0.1 to 15 hr⁻¹ (v/v), and
32 overall hydrogen consumption ranges from 500 to 2500 SCF per barrel
33 of liquid hydrocarbon feed.

- 1 16. The process of claim 1, in which the hydroprocessed effluent of
2 step (b) is reduced in pressure, then heated to a constant temperature
3 before proceeding to step (c).