

MULTI-STAGE HYDROCRACKER WITH KEROSENE RECYCLEFIELD OF THE INVENTION

This invention relates to a multi-stage hydrocracking process in which light products from the first stage, such as naphtha, kerosene and diesel, are joined with naphtha, kerosene and diesel from other sources and recycled from fractionation to a second stage (or subsequent stage) hydrocracker in order to produce lighter products, such as gas and naphtha.

BACKGROUND OF THE INVENTION

Historically, there has been little interest in cracking kerosene or other light products to even lighter products. In the United States, there is little demand for gas or other very light volatile products. Bottoms materials are usually the material recycled in two-stage hydrocracking as practiced in the United States. There is, however, a demand for products such as LPG and LNG in Asia.

Although there has been demand for very light products in some parts of the world, there was a belief by many experts that light products would not crack in most reactors (using conventional hydrocracking catalysts as opposed to FCC catalysts) because they are in the vapor phase as opposed to the liquid phase. This belief apparently originated due to the fact that the environment in a single-stage hydrocracker, in the presence of H_2S and NH_3 , is not conducive to cracking of light products.

The concept of recycling bottoms material back to an initial hydrocracking stage (rather than a second hydrocracking stage) is well known. U.S. Pat. No. 6,261,441 (Gentry et al.) discloses recycling of bottoms material which has been hydrocracked and dewaxed back to a hydrocracker.

1 U.S. Pat. No. 5,447,621 (Hunter) discloses a middle distillate upgrading
2 process. A middle distillate side stream of a conventional single-stage
3 hydrocracking process is circulated to a hydrotreating stage, such as an
4 aromatics saturation reactor and/or a catalytic dewaxing reactor in order to
5 effect middle distillate upgrade. The upgraded product is then finished in a
6 fractionation stage side-stripper column. This invention discloses passing
7 middle distillate to a hydrotreating stage. The middle distillates are being
8 upgraded, not cracked, as in the instant invention.

9
10 U.S. Pat. No. 4,789,457 (Fischer et al.) discloses a process in which a highly
11 aromatic substantially dealkylated feedstock is processed directly to high
12 octane gasoline by hydrocracking over a catalyst preferably comprising a
13 large pore zeolite such as zeolite Y, in addition to a hydrogenation-
14 dehydrogenation component. The feedstock is preferably a light cycle oil.
15 Light cycle oil is heavier than the kerosene and naphtha cracked in the instant
16 invention, and only one hydrocracking stage is employed in Fischer et al.

17 18 SUMMARY OF THE INVENTION

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20 The Applicants have found that in the environment of a clean second-stage
21 hydrocracker, with heteroatoms removed, light products will crack. The
22 examples demonstrate that the net yield of kerosene decreased when
23 recycled to the second stage on a raw feed blend basis, while the qualities of
24 the middle distillates remained the same. Recycling the kerosene to the
25 second stage increased the yield of 170-350°F reformer naphtha, the product
26 most highly valued by the customer.

27
28 The invention disclosed herein is a process for the production of light
29 products, such as gas and naphtha, by processing kerosene in a second
30 stage (or a subsequent stage) of a multi-stage hydrocracker. Kerosene,
31 diesel and naphtha from other sources are included in the recycle, and
32 subsequent hydroprocessing stages are maintained at lower pressures than
33 the initial hydroprocessing stage. This results in cost savings.

1 The instant invention is summarized as follows:

2

3 A method for hydroprocessing a hydrocarbon feedstock, the method
4 employing multiple hydroprocessing zones within a single reaction loop and
5 comprising the following steps:

6

7 (a) passing a hydrocarbonaceous feedstock to a first hydroprocessing zone
8 having one or more beds containing hydroprocessing catalyst, the
9 hydroprocessing zone being maintained at hydroprocessing conditions,
10 wherein the feedstock is contacted with catalyst and hydrogen to
11 produce a vapor stream and a liquid stream as effluent;

12

13 (b) removing the vapor stream of step (a), which comprises hydrogen,
14 hydrogen sulfide and light hydrocarbonaceous gases overhead;

15

16 (c) combining the liquid stream of step (b) with the liquid effluent from other
17 hydroprocessing zones;

18

19 (d) passing the liquid stream of step (c), which comprises
20 hydrocarbonaceous compounds boiling in approximately the same range
21 of the hydrocarbonaceous feedstock, to fractionation;

22

23 (e) separating the liquid stream of step (d), in fractionation, into gas,
24 naphtha, kerosene and diesel fractions, in addition to the bottoms
25 fraction;

26

27 (f) passing the bottoms fraction of step (e) to further processing or recycling
28 to one or more of the other hydroprocessing zones of step (c);

29

30 (g) passing one or more of the naphtha, kerosene and diesel fractions to
31 further processing as products or recycling one or more of the fractions
32 to one or more of the other hydroprocessing zones of step (c) the
33 kerosene, naphtha, and diesel fractions being in combination with

1 kerosene, naphtha and diesel fractions from other sources, said
2 hydroprocessing zones or zones being maintained at hydroprocessing
3 conditions and at lower pressure than the first hydroprocessing zone,
4 and possessing an environment substantially free of H₂S, NH₃, or other
5 heteroatom contaminants;

6

7 (h) passing the effluent of step (g) to fractionation; and

8

9 (i) recovering in fractionation an increased amount of gas and naphtha, in
10 the fractionation stage of step (h) than in the fractionation step of
11 step (e).

12

13 BRIEF DESCRIPTION OF THE DRAWING

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15 The Figure illustrates a two-stage hydrocracking process having the capability
16 for recycle of bottoms fractions, diesel fractions, kerosene fraction or naphtha
17 fractions to the second reactor stage.

18

19 DETAILED DESCRIPTION OF THE INVENTION

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21 Preheated oil feed in stream 1 is mixed with hydrogen in stream 2 prior to its
22 entrance into first stage or primary hydroprocessing zone 10. This
23 hydroprocessing zone is preferably a downflow, fixed bed reactor. This
24 reactor contains multiple beds of hydroprocessing catalysts. At least one bed
25 contains hydrocracking catalyst.

26

27 The effluent 3 of the first stage reactor, which has been hydrotreated and
28 partially hydrocracked, comprises a liquid stream and a vapor stream. The
29 vapor stream 3(a) is removed overhead. It comprises hydrogen, hydrogen
30 sulfide and light hydrocarbonaceous gases. The liquid stream 3(b) is
31 combined with the liquid effluent from other process zones, represented by
32 stream 4. Stream 3(b) and stream 4 are combined to create stream 5.
33 Stream 5 is passed to the fractionation unit 30, where it is separated into gas

1 stream 6, naphtha stream 7, kerosene stream 8, diesel stream 9, and bottoms
2 stream 14. The naphtha product may alternately be recycled, in whole or in
3 part, through stream 11 to stream 15, and ultimately to second stage reactor
4 20. Kerosene product may alternately be recycled, in whole or in part,
5 through stream 12 to stream 15, and ultimately to second stage reactor 20.
6 Diesel product may be alternately recycled, in whole or in part, through stream
7 13 to stream 15, and ultimately to second stage reactor 20. Bottoms material
8 in stream 14 may be passed to further processing (in stream 14a) or,
9 alternately, may be recycled in stream 14(b) to second reactor 20. Second
10 reactor 20 represents hydroprocessing zones subsequent to the first
11 hydroprocessing zone. Each of these zones possesses an environment
12 substantially free of H_2S , NH_3 or other heteroatom components.

13

14 Feeds

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16 A wide variety of hydrocarbon feeds may be used in the instant invention.
17 Typical feedstocks include any heavy or synthetic oil fraction or process
18 stream having a boiling point above 392°F (200°C). Such feedstocks include
19 vacuum gas oils, heavy atmospheric gas oil, delayed coker gas oil, visbreaker
20 gas oil demetallized oils, vacuum residua, atmospheric residua, deasphalted
21 oil, Fischer-Tropsch streams, and FCC streams.

22

23 Products

24

25 Although emphasis is placed on the increased production of gas and naphtha,
26 the process of this invention is also useful in the production of middle distillate
27 fractions boiling in the range of about 250-700°F (121-371°C). A middle
28 distillate fraction is defined as having an approximate boiling range from about
29 250°F to 700°F. At least 75 vol %, preferably 85 vol %, of the components of
30 the middle distillate have a normal boiling point of greater than 250°F. At
31 least about 75 vol %, preferably 85 vol %, of the components of the middle
32 distillate have a normal boiling point of less than 700°F. The term "middle
33 distillate" includes the diesel, jet fuel and kerosene boiling range fractions.

1 The kerosene or jet fuel boiling point range refers to the range between 280°F
2 and 525°F (38-274°C). The term "diesel boiling range" refers to hydrocarbons
3 boiling in the range from 250°F to 700°F (121-371°C).

4
5 Gasoline and naphtha production is emphasized in the process of this
6 invention. Gasoline or naphtha normally boils in the range below 400°F
7 (204°C), or C₁₀-. Boiling ranges of various product fractions recovered in any
8 particular refinery will vary with such factors as the characteristics of the crude
9 oil source, local refinery markets, and product prices.

10

11 Heavy hydrotreated gas oil, another product of this invention, usually boils in
12 the range from 550°F to 700°F.

13

14 Conditions

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16 Hydroprocessing conditions is a general term which refers primarily in this
17 application to hydrocracking or hydrotreating, preferably hydrocracking. The
18 first stage reactor, as depicted in Figure 1, is a partial conversion
19 hydrocracker.

20

21 Typical hydrocracking conditions include a reaction temperature of from
22 400°F-950°F (204°C-510°C), preferably 650°F-850°F (343°C-454°C).

23 Reaction pressure ranges from 500 to 5000 psig (3.5-4.5 MPa), preferably
24 1500-3500 psig (10.4-24.2 MPa). LHSV ranges from 0.1 to 15 hr⁻¹ (v/v),
25 preferably 0.25-2.5 hr⁻¹. Hydrogen consumption ranges from 500 to
26 2500 SCF per barrel of liquid hydrocarbon feed (89.1-445m³ H₂/m³ feed).

27 Reactors subsequent to the first hydroprocessing reactor are operated at a
28 pressure at least 100 psig lower than that of the first reactor, and preferably
29 from 500 to 1000 psig lower than the first reactor.

30

1 Catalyst

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3 Each hydroprocessing zone may contain only one catalyst, or several
4 catalysts in combination.

5

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

22

23 Hydrotreating catalyst usually is designed to remove sulfur and nitrogen and
24 provide a degree of aromatic saturation. It will typically be a composite of a
25 Group VI metal or compound thereof, and a Group VIII metal or compound
26 thereof supported on a porous refractory base such as alumina. Examples of
27 hydrotreating catalysts are alumina supported cobalt-molybdenum, nickel
28 sulfide, nickel-tungsten, cobalt-tungsten and nickel-molybdenum. Typically,
29 such hydrotreating catalysts are presulfided.

30

31 Catalyst selection is dictated by process needs and product specifications. In
32 particular, a noble catalyst may be used in the second stage when there is a
33 low amount of H₂S present.

1 The Examples below demonstrate the relative effectiveness of recycling
2 kerosene to produce lighter products of high quality, as opposed to not
3 recycling kerosene.

4

5

EXAMPLE

6

7 The "recycle" of kerosene was simulated by passing kerosene from the first
8 hydrocracking stage over the catalyst in the second hydrocracking stage. The
9 first stage kerosene possessed a smoke point of 14 mm and 25 LV%
10 aromatics. Net yields from the runs where kerosene was "recycled" have
11 been calculated by deducting the supplemental kerosene feed from the gross,
12 measured kerosene yield (gross weight of kerosene product-weight of
13 kerosene "recycled" = net yield of kerosene product).

14

15 In kerosene recycle mode, a base metal zeolite hydrocracking catalyst
16 cracked a substantial fraction of the kerosene to naphtha and gas (see
17 Tables 1 and 2). The net yield of kerosene decreased on a raw feed blend
18 basis and the qualities of the middle distillates remained the same. Recycling
19 the kerosene to the second stage did increase the yield of 170-350°F reformer
20 naphtha, a product in most demand by the customer.

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TABLE 1

Two-Stage Hydrocracking of
Vacuum Gas Oil / Hydrocracking Gas Oil /
Light Cycle Oil Feed Blend Using Hydrocracking Catalyst

Run Hours	600-624	
Reactor 1 Temp, °F	725	
Reactor 2 Temp, °F	669	
Overall LHSV, hr ⁻¹	1.00	
Per Pass Conversion	58	
Total Pressure, PSIG	2297	
No Loss Prod. Yields	Wt. %	Vol. %
C ₁	0.13	
C ₂	0.18	
C ₃	0.56	
iC ₄	0.94	1.62
nC ₄	0.63	1.06
C ₅ -170°F	3.43	5.04
170-350°F	13.04	16.48
350-550°F	29.99	33.44
550-RCP	15.57	16.92
Recycle Bleed	34.84	38.17
Recycle Cut Point, °F	656	
Total C ₄ -	2.44	
Total C ₅ +	96.87	110.04
Closure	99.6	//
Fractionator Bottoms Nitrogen, ppm	24.5	

TABLE 2

1			
2			
3	Two-Stage Hydrocracking of		
4	Vacuum Gas Oil / Hydrocracked Gas Oil / Light Cycle Oil		
5	<u>Feed Blend Using Hydrocracking Catalyst, with "Kerosene Recycle"</u>		
6			
7	Hours	816-840	
8	Reactor 1 Temperature, °F	725	
9	Reactor 2 Temperature, °F	691	
10	LHSV, 1/Hr	1.00	
11	Per Pass Conversion, %	60	
12	Total Pressure, psig	2294	
13			
14	No Loss Product Yields	Wt. %	Vol %
15	C ₁	0.13	
16	C ₂	0.20	
17	C ₃	0.80	
18	iC ₄	1.80	
19	nC ₄	0.99	
20	C ₅ -170°F	6.4	9.5
21	170-350°F	18.0	22.8
22	350-550°F	24.0	26.8
23	550-650°F	15.3	16.6
24	650°F+	32.4	35.3
25	Recycle cut point	650°F	
26	Total C ₅ +	96.1	111.0
27	Total C ₄ -	3.72	
28	Chemical H ₂ Consumption, SCF/B	2080	
29	Closure, %	99.7	
30			
31	Fractionator Bottoms Nitrogen, ppm	28	

1 WHAT IS CLAIMED IS:

2

3 1. A method for hydroprocessing a hydrocarbon feedstock, the method
4 employing multiple hydroprocessing zones within a single reaction loop
5 and comprising the following steps:

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7 (a) passing a hydrocarbonaceous feedstock to a first hydroprocessing
8 zone having one or more beds containing hydroprocessing
9 catalyst, the hydroprocessing zone being maintained at
10 hydroprocessing conditions, wherein the feedstock is contacted
11 with catalyst and hydrogen to produce a vapor stream and a liquid
12 stream as effluent;

13

14 (b) removing the vapor stream of step (a), which comprises hydrogen,
15 hydrogen sulfide and light hydrocarbonaceous gases overhead;

16

17 (c) combining the liquid stream of step (b) with the liquid effluent from
18 other hydroprocessing zones;

19

20 (d) passing the liquid stream of step (c), which comprises
21 hydrocarbonaceous compounds boiling in approximately the same
22 range of the hydrocarbonaceous feedstock, to fractionation;

23

24 (e) separating the liquid stream of step (d), in fractionation, into gas,
25 naphtha, kerosene and diesel fractions, in addition to the bottoms
26 fraction;

27

28 (f) passing the bottoms fraction of step (e) to further processing or
29 recycling to one or more of the other hydroprocessing zones of
30 step (c);

31

32 (g) passing one or more of the naphtha, kerosene and diesel fractions
33 to further processing as products or recycling one or more of the

- 1 fractions to one or more of the other hydroprocessing zones of
2 step (c), the kerosene, naphtha or diesel fractions being in
3 combination with kerosene, naphtha or diesel fractions from other
4 sources, said hydroprocessing zone or zones being maintained at
5 hydroprocessing conditions and at lower pressure than the first
6 hydroprocessing zone, and possessing an environment
7 substantially free of H_2S , NH_3 , or other heteroatom contaminants;
8
- 9 (h) passing the effluent of step (g) to fractionation;
10
- 11 (i) recovering in fractionation an increased amount of gas and
12 naphtha, and a decreased amount of kerosene, in the fractionation
13 stage of step (h) than in the fractionation step of step (e).
14
- 15 2. The process of claim 1, wherein the pressure in the subsequent zone or
16 zones of claim 1, step (g), are at least 100 psi lower than the pressure in
17 the initial zone.
18
- 19 3. The process of claim 2, wherein the pressure in the subsequent zone or
20 zones of claim 1 is from 500 to 1000 psig lower than the pressure in the
21 initial zone.
22
- 23 4. The process of claim 1, wherein at least one bed in each
24 hydroprocessing zone contains hydrocracking catalyst.
25
- 26 5. The process of claim 1, wherein the hydroprocessing conditions of
27 claim 1, step (a), and claim 1, step (g), comprise a reaction temperature
28 of from 400°F-950°F (204°C-510°C), a reaction pressure in the range
29 from 500 to 5000 psig (3.5-34.5 MPa), an LHSV in the range from 0.1 to
30 15 hr^{-1} (v/v), and hydrogen consumption in the range from 500 to
31 2500 scf per barrel of liquid hydrocarbon feed (89.1-445 $m^3 H_2/m^3$ feed).
32

- 1 6. The process of claim 5, wherein the hydroprocessing conditions of
2 claim 1, step (a), and claim 1, step (g), preferably comprise a
3 temperature in the range from 650°F-850°F (343°C-454°C), reaction
4 pressure in the range from 1500-3500 psig (10.4-24.2 MPa), LHSV in
5 the range from 0.25 to 2.5 hr⁻¹, and hydrogen consumption in the range
6 from 500 to 2500 scf per barrel of liquid hydrocarbon feed (89.1-445 m³
7 H₂/m³ feed).
8
- 9 7. The process of claim 1, wherein the feed to claim 1, step (a), comprises
10 hydrocarbons boiling above 392°F(200°C).
11
- 12 8. The process of claim 7, wherein the feed is selected from the group
13 consisting of vacuum gas oil, heavy atmospheric gas oil, delayed coker
14 gas oil, visbreaker gas oil, demetallized oils, FCC light cycle oil, vacuum
15 residua deasphalted oil, Fischer-Tropsch streams, and FCC streams.
16
- 17 9. The process of claim 1, wherein the hydroprocessing catalysts of the
18 first hydroprocessing zone of claim 1, step (a), and the hydroprocessing
19 zone of claim 1, step (g), comprise a cracking component and a
20 hydrogenation component.
21
- 22 10. The process of claim 9, wherein the hydrogenation component is
23 selected from Group VI, Group VII or Group VIII metals.
24
- 25 11. The process of claim 10, wherein the hydrogenation component is
26 selected from the group consisting of Ni, Mo, W, Pt and Pd or
27 combinations thereof.
28
- 29 12. The process of claim 10, wherein the Group VI, Group VII or Group VIII
30 metals may exist as either sulfides or oxides.
31
- 32 13. The process of claim 10, wherein the hydrogenation component
33 comprises 5 to 40 wt% of the catalyst.

- 1 14. The process of claim 11, wherein noble metals comprise from about
2 0.1 wt% to about 2 wt% of the catalyst.
3
- 4 15. The process of claim 9, wherein the cracking component may be
5 amorphous or zeolitic.
6
- 7 16. The process of claim 15, wherein the zeolitic component is selected from
8 the group consisting of Y, USY, REX, and REY zeolites.
9
- 10 17. The process of claim 1, step (i), wherein an increased amount of
11 naphtha boiling in the range of 170-350°F is recovered.