

1 PROCESS FOR REVERSE STAGING IN
2 HYDROPROCESSING REACTOR SYSTEMS

3
4 1. FIELD OF THE INVENTION

5
6 The present invention relates to the field of hydroprocessing. In particular,
7 the present invention relates to hydroprocessing to obtain high conversions,
8 product selectivity and selective hydrotreating of specific boiling range
9 products.

10
11 II. BACKGROUND OF THE INVENTION

12
13 There are two conventional approaches in the petroleum
14 hydroprocessing/hydrotreating art to obtain high conversions. "High
15 conversions" includes sulfur removal, nitrogen removal, hydrocracking,
16 ramsbottom carbon reduction, and the like. The two conventional processes
17 include (a) a long residence time or low space velocity reactors, or (b) a
18 separate reactor loop for the high conversion step after feed impurities are
19 reduced in an initial reactor loop.

20
21 The second approach using separate reactor loop is effective. This is
22 because the eliminated feed impurity byproducts such as H_2S , NH_3 , are not
23 present in the typically high concentrations that exist in the first reaction loop.
24 There presence in high concentrations would tend to inhibit reaction rates in
25 the second reaction loop.

26
27 There exists some conventional approaches in the art for obtaining good
28 product selectivity. "Selectivity" includes obtaining a preferential yield of
29 certain boiling range materials. These conventional processes include
30 (a) recycling the undesirable products for reprocessing with the fresh feed, or

1 (b) reprocessing the undesirable products in a separate reaction loop.
2 Typical approaches in the art to selective hydrotreating of specific boiling
3 range products include (a) overtreating of the entire feed to the point where
4 the most difficult product specification is met, or (b) treating of the whole feed
5 to a lesser extent followed by a separate hydrotreating of particular product
6 cuts to meet the most difficult specifications.

7
8 It would be desirable to have a hydroprocessing process which achieved
9 higher conversion or deeper treating processing while avoiding the
10 drawbacks of known processes.

11

12 III. SUMMARY OF THE INVENTION

13

14 The present invention serves to accomplish these objectives in a single
15 reaction loop including lower costs than multiple loops, while maintaining the
16 advantages of a multiple loop system including higher reaction rates or
17 catalysts tailored for pretreated feeds.

18

19 The present invention includes a process for reverse staging to obtain high
20 conversion, selective hydrotreating and product selectivity in a
21 hydroprocessing reactor system including performing in a single reactor loop
22 a higher conversion or deeper treating processing in a top bed(s) of a reactor
23 or in the lead reactor in a series reactor loop and performing the general feed
24 processing in the reactor zones that follow.

25

IV. BRIEF DESCRIPTION OF THE DRAWINGS

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27 FIG. 1 depicts one embodiment of a flow diagram of the process of the
28 invention utilizing a common vessel for housing the different treatment zones.

29

1 FIG. 2 depicts an alternate embodiment of a flow diagram of the process of
2 the invention utilizing separate vessels for housing the different treatment
3 zones.

4

5 **V. DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS**

6

7 **A. Overview of the Process: Upper and Lower Reaction Zones**

8

9 The invention is a method of reverse stage hydrotreating a hydrocarbon feed
10 to obtain high conversion, selective hydrotreating and product selectivity in a
11 hydroprocessing reactor system. The method includes passing a
12 hydrocarbon feed to a first hydrotreating zone, e.g., a denitrification and
13 desulfurization zone. In that zone, the hydrocarbon feed is contacted at
14 hydrotreating conditions, e.g., denitrification and desulfurization conditions,
15 with a hydrotreating catalyst, e.g., a denitrification and desulfurization
16 catalyst. After the contacting, a denitrification and desulfurization zone
17 effluent is recovered.

18

19 The denitrification and desulfurization zone effluent is then passed to a
20 purification/cooling zone (or termed a "NH₃ and H₂S and cooling zone").
21 Ammonia and H₂S are removed, typically by water scrubbing. The effluent is
22 cooled by any conventional means, e.g., by heat exchanger. Recovered from
23 the purification/cooling zone is a hydrogen/light hydrocarbon stream from the
24 top and a liquid stream containing dissolved gases from the bottom. The
25 hydrogen/light hydrocarbon stream is optionally passed to a second H₂S
26 removal zone, typically using an amine adsorbent for H₂S removal. The
27 recovered effluent from the optional H₂S removal zone is optionally passed to
28 a second hydrotreating zone, e.g., the hydrocracking zone discussed below.

29

1 The liquid stream containing dissolved gases is passed to a separation zone.
2 Any conventional separation may be used, typically distillation. A light
3 product and other fractions selected from a liquid bottoms, one or more side-
4 or mid-cuts, and mixtures thereof, are recovered. The other fractions, i.e.,
5 liquid bottoms and/or one or more side- or mid-cuts, are passed to a second
6 hydrotreating zone, e.g., a hydrocracking zone. There, at hydrocracking
7 conditions, the liquid bottoms and/or one or more side- or mid-cuts are
8 contacted with a hydrocracking catalyst. A hydrocracking zone effluent is
9 then recovered. The hydrocracking zone effluent is then passed to the first
10 hydrotreating zone, in one embodiment, a denitrification and desulfurization
11 zone.

12

13 The use of the two reaction zones can be varied in this invention. That is, the
14 first and second hydrotreating or reaction zone may each be a hydrocracking
15 zone or a denitrification and desulfurization zone. In one embodiment of the
16 invention, the lower zone which the fresh feed first contacts is a denitrification
17 and desulfurization zone. The upper feed is a hydrocracking zone. In
18 another embodiment, the reverse is true. Alternatively, each zone may both
19 be either a hydrocracking zone or each a denitrification and desulfurization
20 zone. Each may also be a combination or mixture of a hydrocracking zone
21 and a denitrification and desulfurization zone.

22

23 B. Advantages of Process of the Invention

24

25 The present invention provides a single reaction loop. This single reaction
26 loop method lowers costs as compared to the use of multiple reaction loops.
27 Yet, the single reaction loop of the invention maintains the advantages of
28 higher reaction rates or catalyst tailored for pretreated feeds of a multiple
29 reaction loop system. The present invention accomplishes the final
30 processing in the upper reaction zone or top bed or beds of a reactor or

1 reactors in series while performing the general feed processing in the lower
2 reaction zones that follow.

3

4 Another advantage of a series configuration rather than a parallel reactor
5 configuration for the initial conversion and one for the high conversion step is
6 that gas circulation is minimized thereby reducing both investment and
7 operating costs. The capital cost is lower due to smaller equipment and
8 piping. Operating costs are lower due to less compressor power to
9 recirculate gas. The gas circulation is reduced relative to initial processing in
10 a separate loop or parallel reactor of the same loop because (a) the high
11 conversion effluent from the top reaction zone serves as a partial heat sink
12 and thereby reduces the quench requirements for the initial processing in the
13 zones which follow, (b) the unused hydrogen in the high conversion effluent
14 from the top zone serves as a partial source of hydrogen for the initial
15 processing in the zones which follow, and (c) the high conversion effluent
16 from the top reaction zone helps to provide good distribution of the fresh feed
17 and hydrogen for reaction on the catalyst in the zones which follow. Thus,
18 the advantages of using a single loop are reduced investment cost and
19 operating costs by not duplicating similar pieces of equipment in two separate
20 loops, i.e., one for the initial processing and one for the high conversion step.

21

22 Advantages of processing the pretreated hydrocarbon in upper reaction zone
23 or top bed separate from the fresh feed include (a) the top bed catalysts are
24 not contaminated with feed impurities, (b) the reaction rate in the top beds is
25 not inhibited by substantial quantities of hydrotreating byproducts, e.g., NH_3
26 and H_2S , and (c) hydrogen partial pressures are maximized for the finishing
27 processes.

28

1 In an optional embodiment in the case of residuum processing, the present
2 process can also provide benefits in the lower reaction zones which includes
3 reduced pulsation tendency.

4
5 **C. Feedstocks and Products**

6
7 Feedstocks suitable for use in the invention and desired products obtained
8 include any conventional or known hydrocracking/hydroprocessing
9 feedstocks and products. The feedstocks and desired products for the
10 instant process include those disclosed in U.S. Patent Nos. 5,277,793;
11 5,232,577; 5,073,530; 4,430,203; and 4,404,088 which are incorporated
12 herein by reference. In one preferable embodiment, the hydrocarbon feed is
13 selected from a residuum, a vacuum gas oil, middle-distillates, and mixtures
14 thereof.

15
16 **D. Reaction Conditions and Catalysts**

17
18 Suitable hydrocracking and hydroprocessing catalysts and reaction
19 conditions include any conventional or known catalysts and reaction
20 conditions. The catalysts and reaction conditions suitable for the instant
21 process include those disclosed in U.S. Patent Nos. 5,277,793; 5,232,577;
22 5,073,530; 4,430,203; and 4,404,088 which are incorporated herein by
23 reference. Where the reaction zone is a denitrification and/or desulfurization
24 zone, the contacting occurs at denitrification and/or desulfurization
25 conditions. Where the reaction zone is a hydrocracking zone, the contacting
26 occurs at hydrocracking conditions.

27
28 When the above-described process is used to hydrotreat feedstocks to
29 remove sulfur and nitrogen impurities, the following process conditions will
30 typically be used: reaction temperature, 400°F-900°F; pressure, 500 to

1 5000 psig; LHSV, 0.5 to 20; and overall hydrogen consumption 300 to
2 2000 scf per barrel of liquid hydrocarbon feed. The hydrotreating catalyst for
3 the beds will typically be a composite of a Group VI metal or compound
4 thereof, and a Group VIII metal or compound thereof supported on a porous
5 refractory base such as alumina. Examples of hydrotreating catalysts are
6 alumina supported cobalt-molybdenum, nickel sulfide, tungsten-nickel sulfide,
7 cobalt molybdate and nickel molybdate.

8
9 Correspondingly, when the process is used to hydrocrack feedstocks, the
10 following operating conditions will normally prevail: reaction temperature,
11 400°F-950°F; reaction pressure 500 to 5000 psig; LHSV, 0.1 to 15; and
12 hydrogen consumption 500 to 2500 scf per barrel of liquid hydrocarbon feed.
13 The hydrocracking catalysts used for the beds will typically be a Group VI,
14 Group VII, or Group VIII metal or oxides or sulfides thereof supported on a
15 porous refractory base such as silica or alumina. Examples of hydrocracking
16 catalysts are oxides or sulfides of Mo, W, V, and Cr supported on such
17 bases.

18
19 Generally, where the reaction zone is a denitrification and/or desulfurization
20 zone, the catalyst is any catalyst which will catalyze denitrification and/or
21 desulfurization at denitrification and/or desulfurization conditions. Where the
22 reaction zone is a hydrocracking zone, the catalyst is any catalyst which will
23 catalyze hydrocracking at hydrocracking conditions.

24

25 VI. DETAILED DESCRIPTION OF THE DRAWINGS

26

27 Modifications of the process that is shown in the drawings and described in
28 this specification that are obvious to those of ordinary skill in the oil refinery
29 process art are intended to be within the scope of the invention.

30

1 **A. Figure 1**

2

3 As illustrated in the flow diagram of FIG. 1, the catalytic reactions used in this
4 process are accomplished in two reaction zones 3 and 10. Vessel 2 houses
5 both reaction zones 3 and 10. The initial processing is carried out in the
6 second zone 10 and the high conversion processing carried out in the first
7 zone 3. The flow scheme optionally includes other features which are
8 common in hydroprocessing units such as preheating of liquid and gas feeds
9 to the reactors (preheaters not shown), NH_3 and H_2S removal and effluent
10 cooling and separation zone 20, optional recycle gas purification zone 31,
11 and recirculation streams 30 and 32, and product separation and distillation
12 zone 40. Liquid bottoms stream 50, and/or side- or mid-cut 52, from
13 distillation zone 40 are joined as stream 54. Stream 54 is passed to reaction
14 zone 3. Make-up hydrogen stream 60 is added to gas recirculation stream 32
15 (also termed "hydrogen/light hydrocarbon stream 30" or " H_2S removal zone
16 effluent 32"). Alternatively, make-up hydrogen stream 70 is added to feed
17 stream 1 instead of, or in addition to, adding make-up hydrogen to stream 32.
18

19 Hydrocracking or deeper hydrotreating takes place in reaction zone 3
20 depending on the type of catalyst used in that zone. The effluent 65 from
21 reaction zones passes to reaction zone 10. Fresh feed 1 is introduced at an
22 intermediate point between reactor beds 3 and 10. It is processed in the
23 presence of the effluent 65 from the upper reaction zone 3. Effluent 65
24 assists in distribution of feed stream 1 through reaction zone 10. Effluent 65
25 also acts as a heat-sink for the exothermic reaction in reaction zone 10.
26

27 The effluent 15 from the lower zone 10 is treated for NH_3 and H_2S removal in
28 zone 20. Conventional methods, typically water washing, is utilized for the
29 NH_3 and H_2S removal. Zone 20 is also a cooling and separation zone
30 producing a gas stream 30 and a liquid stream containing dissolved

1 gases 35. Conventional processing is used for the interrelationships of the
2 NH_3 and H_2S removal and cooling and separation processes in zone 20.
3 Zone 20 may include multiple units or sub-zones according to conventional
4 means for accomplishing the NH_3 and H_2S removal and cooling and
5 separation. A hydrogen rich gas stream 32 is recycled back to the reactors
6 and then mixed with make-up hydrogen stream 60. Alternatively, or in
7 addition to mixing make-up hydrogen stream 60 with hydrogen rich gas
8 stream 32, make-up hydrogen stream 70 is mixed with oil feed stream 1. The
9 recycle gas in stream 30 is optionally purified, e.g., by amine adsorbent for
10 H_2S removal, in zone 31 before recirculation to the reactors. The recycle gas
11 of stream 30 (or stream 32 if further purified in zone 31) is optionally fed to
12 stream 54 for feeding to first reaction zone 3 or is passed, as stream 34, to
13 feed stream 1 for feeding to second reaction zone 10.

14

15 B. Figure 2

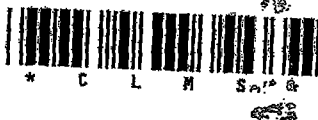
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17 The description of FIG. 2 is the same as for Figure 1 above, except for the
18 following differences. In Figure 1, a common vessel houses the reaction
19 zones. In Figure 2, separate vessels 2 and 9 house reaction zones 3 and 10,
20 respectively. In Figure 1, there is a recycle gas purification zone 31. In
21 Figure 2, this unit is omitted.

VII. CLAIMS

WHAT IS CLAIMED IS:

1. A method of reverse stage hydrotreating a hydrocarbon feed to obtain high conversion, selective hydrotreating and product selectivity in a hydroprocessing reactor system, said method comprising:
 - a. Passing a hydrocarbon feed selected from a residuum, a vacuum gas oil, middle distillate, and mixtures thereof to a denitrification and desulfurization zone; contacting said hydrocarbon feed at a temperature of about 400°F to about 900°F; a pressure of about 500 psig to about 5000 psig; a flow rate of about 0.5 LHSV to about 20 LHSV; and an overall hydrogen consumption of about 300 to about 2000 scf per barrel of liquid hydrocarbon feed, with a denitrification and desulfurization catalyst; and recovering a denitrification and desulfurization zone effluent therefrom;
 - b. Passing said denitrification and desulfurization zone effluent to a purification/cooling zone for removal of NH_3 and H_2S and cooling, and recovering from said purification/cooling zone a hydrogen/light hydrocarbon stream and a liquid stream containing dissolved gases;
 - c. Passing said liquid stream containing dissolved gases to a separation zone and recovering a light product, a liquid bottoms, and at least one side-cut product therefrom;
 - d. Passing said liquid bottoms and said side-cut product and said hydrogen/light hydrocarbon stream from step (b) to a hydrocracking zone; contacting said liquid bottoms and said



1 side-cut product at a temperature of about 400°F to about 950°F; a
2 pressure of about 500 psig to about 5000 psig; a flow rate of about
3 0.1 LHSV to about 15 LHSV; and an overall hydrogen
4 consumption of about 500 to about 2500 scf per barrel of liquid
5 hydrocarbon feed, with a hydrocracking catalyst; and recovering a
6 hydrocracking zone effluent therefrom; and

7 e. Passing said hydrocracking zone effluent to said denitrification
8 and desulfurization zone.

9 2. A process for reverse staging to obtain high conversion, selective
10 hydrotreating and product selectivity in a hydroprocessing reactor
11 system comprising performing in a single reactor loop a higher
12 conversion or deeper treating processing in an upper reaction zone of a
13 reactor or in the lead reactor in a series reactor loop and performing the
14 general feed processing in the reaction zones that follow.

15 3. The process of claim 2 further comprising feeding make-up hydrogen to
16 said upper reaction zone or the reaction zones that follow.

17 4. The process of claim 2 further comprising:

18 a. Recovering an effluent from said reaction zones that follow and
19 passing said effluent to a cooling zone;

20 b. Recovering from said cooling zone a hydrogen/light hydrocarbon
21 stream and a liquid hydrocarbon stream containing dissolved
22 gases;

23 c. Passing said hydrogen/light hydrocarbon stream to said upper
24 reaction zone; and



- 1 d. Passing said liquid stream containing dissolved gases to a
2 separation zone.
- 3 5. The process of claim 3 wherein said general feed is selected from a
4 residuum, a vacuum gas oil, a middle distillate, and mixtures thereof;
5 and further comprising passing said hydrogen/light hydrocarbon stream
6 in step (b) to a H₂S removal zone prior to passing to said upper reaction
7 zone or lead reactor in step (c).
- 8 6. The process of claim 4 wherein said reactor zones that follow are
9 hydrocracking zones and comprise a hydrocracking catalyst and
10 wherein said hydrocracking zones have a temperature of about 400°F to
11 about 950°F; a pressure of about 500 psig to about 5000 psig; a flow
12 rate of about 0.1 LHSV to about 15 LHSV; and an overall hydrogen
13 consumption of about 500 to about 2500 scf per barrel of liquid
14 hydrocarbon feed.
- 15 7. The process of claim 5 wherein said reactor zones that follow are
16 denitrification and desulfurization zones and said process further
17 comprises contacting in said denitrification and desulfurization zones a
18 denitrification and desulfurization catalyst with a general feed selected
19 from residuum, a vacuum gas oil, middle distillates, and mixtures
20 thereof, at a temperature of about 400°F to about 900°F; a pressure of
21 about 500 psig to about 5000 psig; a flow rate of about 0.5 LHSV to
22 about 20 LHSV; and an overall hydrogen consumption of about 300 to
23 about 2000 scf per barrel of liquid hydrocarbon feed, and further
24 comprises recovering a denitrification and desulfurization zone effluent.



- 1 8. The process of claim 4 wherein said reaction zones that follow are
2 hydrocracking zones and said process further comprises contacting in
3 said hydrocracking zones a hydrocracking catalyst with a general feed
4 selected from residuum, a vacuum gas oil, middle distillates, and
5 mixtures thereof, at a temperature of about 400°F to about 950°F; a
6 pressure of about 500 psig to about 5000 psig; a flow rate of about
7 0.1 LHSV to about 15 LHSV; and an overall hydrogen consumption of
8 about 500 to about 2500 scf per barrel of liquid hydrocarbon feed.
- 9 9. The process of claim 7 wherein said upper reaction zone or lead reactor
10 is a hydrocracking zone and said process further comprises contacting
11 in said hydrocracking zones a hydrocracking catalyst with at least a
12 portion of said denitrification and desulfurization zone effluent, at a
13 temperature of about 400°F to about 950°F; a pressure of about
14 500 psig to about 5000 psig; a flow rate of about 0.1 LHSV to about
15 15 LHSV; and an overall hydrogen consumption of about 500 to about
16 2500 scf per barrel of liquid hydrocarbon feed.
- 17 10. The process of claim 4 wherein said upper reaction zone or lead reactor
18 is a denitrification and desulfurization zone.
- 19 11. The process of claim 9 further comprising:
- 20 a. Passing said denitrification and desulfurization zone effluent to a
21 purification/cooling zone for removal of NH_3 and H_2S and cooling,
22 and recovering from said purification/cooling zone a hydrogen/light
23 hydrocarbon stream and a liquid stream containing dissolved
24 gases;



- 1 b. Passing said liquid stream containing dissolved gases to a
2 separation zone and recovering a light product, a liquid bottoms,
3 and at least one side-cut product therefrom; and
- 4 c. Passing said liquid bottoms and said side-cut product and said
5 hydrogen/light hydrocarbon stream from step (b) to said upper
6 reaction zone.
- 7 12. A method of processing a hydrocarbon feed comprising:
- 8 a. Passing a hydrocarbon feed to a second hydrotreating zone,
9 contacting at hydrotreating conditions said hydrocarbon feed with
10 a second hydrotreating catalyst, and recovering a second
11 hydrotreating zone effluent therefrom;
- 12 b. Passing said hydrotreated product to a vapor-liquid separation
13 zone, and recovering therefrom a light product and other fractions
14 selected from a liquid bottoms, one or more middle cuts, and
15 mixtures thereof;
- 16 c. Passing said other fractions to a first hydrotreating zone,
17 contacting at hydrotreating conditions said hydrocarbon feed with
18 a first hydrotreating catalyst, and recovering a first hydrotreating
19 zone effluent therefrom; and
- 20 d. Passing said first hydrotreating zone effluent to said second
21 hydrotreating zone.
- 22 13. The process of claim 12 further comprising feeding make-up hydrogen
23 to said second hydrotreating zone.
- 24 14. The process of claim 12 further comprising:



- 1 a. Passing said second hydrotreating zone effluent to a NH_3 and H_2S
2 removal and cooling zone;
- 3 b. Recovering from said NH_3 and H_2S removal and cooling zone a
4 hydrogen/light hydrocarbon stream and a liquid hydrocarbon
5 stream containing dissolved gases;
- 6 c. Passing said hydrogen/light hydrocarbon stream to said first
7 hydrotreating zone; and
- 8 d. Passing said liquid hydrocarbon stream containing dissolved
9 gases to said vapor-liquid separation zone.
- 10 15. The process of claim 14 wherein said hydrocarbon feed is selected from
11 a residuum, a vacuum gas oil, middle-distillates, and mixtures thereof.
- 12 16. The process of claim 12 wherein said second hydrotreating zone is a
13 denitrification and desulfurization zone having a temperature of about
14 400°F to about 900°F; a pressure of about 500 psig to about 5000 psig;
15 a flow rate of about 0.5 LHSV to about 20 LHSV; and an overall
16 hydrogen consumption of about 300 to about 2000 scf per barrel of
17 liquid hydrocarbon feed, and wherein said second hydrotreating catalyst
18 comprises a denitrification and desulfurization catalyst.
- 19 17. The process of claim 16 wherein said second hydrotreating zone is a
20 hydrocracking zone.



- 1 18. The process of claim 12 wherein said first hydrotreating zone is a
2 hydrocracking zone having a temperature of about 400°F to about
3 950°F; a pressure of about 500 psig to about 5000 psig; a flow rate of
4 about 0.1 LHSV to about 15 LHSV; and an overall hydrogen
5 consumption of about 500 to about 2500 scf per barrel of liquid
6 hydrocarbon feed, and wherein said first hydrotreating catalyst
7 comprises a hydrocracking catalyst.
- 8 19. The process of claim 12 wherein said first hydrotreating zone is a
9 denitrification and desulfurization zone.

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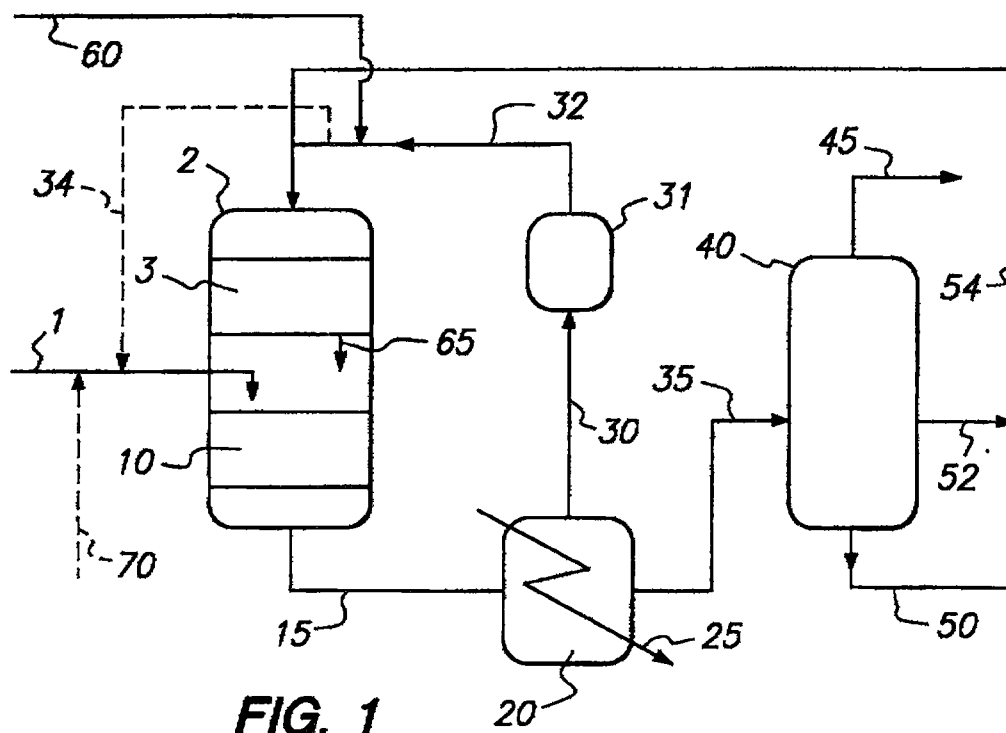


FIG. 1

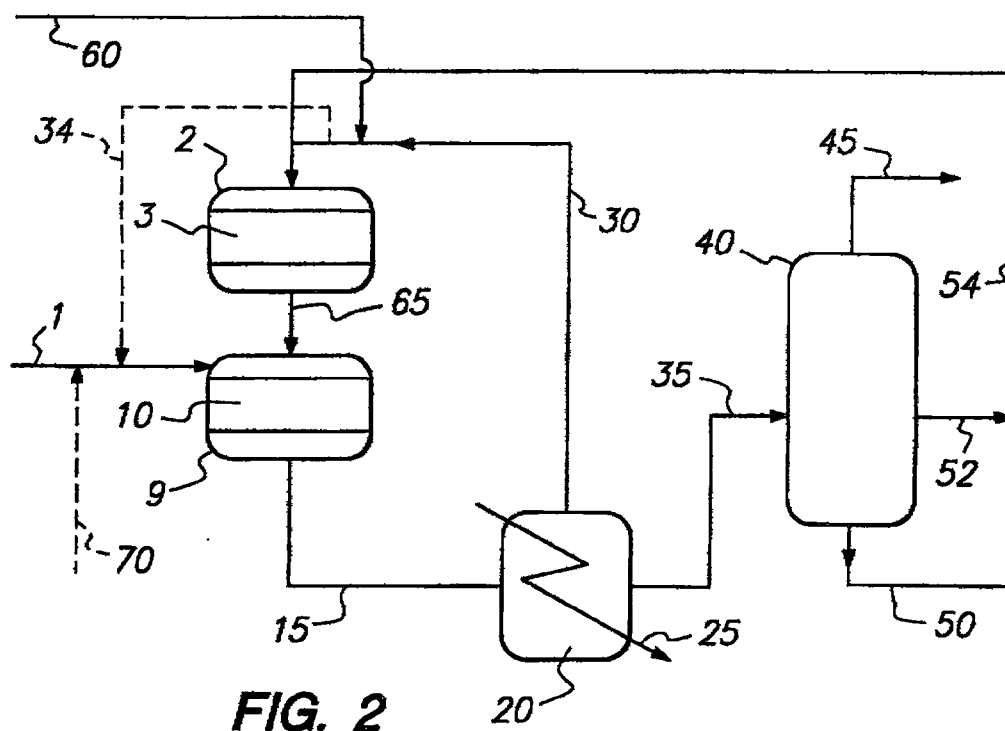


FIG. 2

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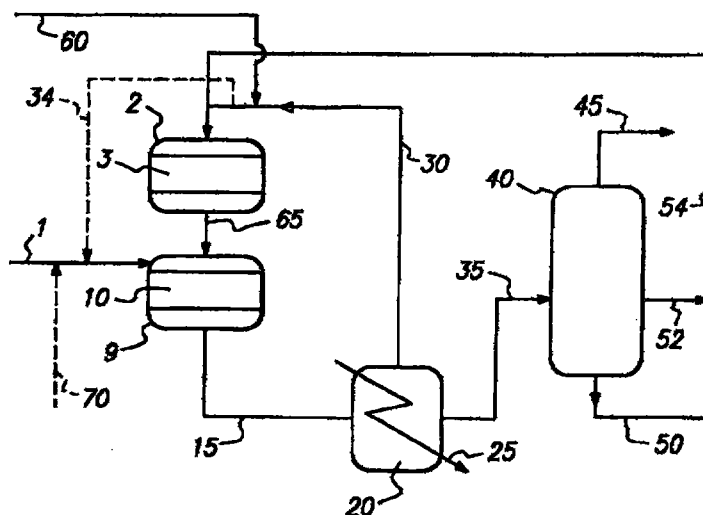
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(57) Abstract

A hydrocarbon feed (1) is passed to a denitrification and desulfurization zone (10); passing said denitrification and desulfurization zone effluent to a purification/cooling zone (20) for removal of NH_3 and H_2S and cooling, and recovering from said purification/cooling zone a hydrogen/light hydrocarbon stream (30) and a liquid stream containing dissolved gases (35); passing said liquid stream containing dissolved gases to a separation zone (40) and recovering a light product (45), a liquid bottoms (50), and at least one side-cut product therefrom (52); passing said liquid bottoms (50) and said side-cut (52) product and said hydrogen/light hydrocarbon stream from step (30) (b) to a hydrocracking or a hydrotreating zone; passing said hydrocracking or hydrotreating zone effluent (65) to said denitrification and desulfurization zone (10).