

PROCESS FOR SELECTIVE HYDROGENATION OF CRACKED HYDROCARBONS

5 BACKGROUND OF THE INVENTION

1. Field Of The Invention

10 This invention relates to a process for the selective hydrogenation of cracked hydrocarbons, more particularly to process sequences for the reduction of fouling in the fractional distillation of light end hydrocarbon components, such as those produced by catalytic cracking, pyrolysis or steam cracking. More particularly still, but not exclusively, the invention relates to
15 process sequences to reduce fouling by use of upstream hydrogenation unit configurations, rather than the multiple hydrogenation unit configurations used in conventional fractional distillation systems.

20 2. Background

Steam crackers can operate on light paraffin feeds such as ethane and propane, or on feedstocks which contain propane and heavier compounds to make olefins. Steam cracking these heavier
25 feedstocks produces many marketable products, notably propylene, isobutylene, butadiene, amylene and pyrolytic gasoline.

In addition to the foregoing, small quantities of undesirable contaminants, such as di- and poly-olefins, and acetylenic
30 compounds are produced. These contaminants may also be produced with olefins from catalytic cracking. These contaminants may cause equipment fouling or interfere with polymerization reactions, in downstream polymerization uses of the products. It is,

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therefore, highly desirable to remove them from the cracked stream in the downstream recovery process.

The recovery of the various olefin products from cracked streams is usually carried out by fractional distillation using a series of distillation steps or columns to separate out the various components. The unit which separates hydrocarbons with one carbon atom (C₁) and lighter fraction is referred to as the "demethanizer". The unit which separates hydrocarbons with two carbon atoms (C₂) from the heavier components is referred to as the "deethanizer". The unit which separates the hydrocarbon fraction with three carbon atoms (C₃) from the heavier components is referred to as the "depropanizer". The unit which separates the hydrocarbon fraction with four carbon atoms (C₄) from the heavier components is referred to as the "debutanizer." The residual heavier components having a higher carbon number fraction (C₅⁺) may be used as gasoline or recycled back to the steam cracker. The various fractionation units may be arranged in a variety of sequences in order to provide desired results based upon various feedstocks. To that end, a sequence which uses the demethanizer first is commonly referred to as the "front-end demethanizer" sequence. Similarly, when the deethanizer is used first, it is commonly referred to as the "front-end deethanizer" sequence. And, when the depropanizer is used first, it is commonly referred to as "front-end depropanizer" sequence.

In all of the sequences, the gases leaving the steam cracker are quenched and have their acid gas removed. At this point, various flow sequences may optionally be used. In the conventional front-end demethanizer sequence, the quenched and acid-free gases containing hydrocarbons having one to five or more carbon atoms per molecule (C₁ to C₅⁺) first enter a demethanizer, where hydrogen and C₁ are removed. This tower

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operates at relatively low temperatures (typically ranging from about -100°C to about 25°C) and therefore has a low tendency to foul. The heavy ends exiting the demethanizer, consists of C₂ to C₅⁺ molecules. These heavy ends then are routed to a deethanizer where the C₂ components are taken over the top and the C₃ to C₅⁺ compounds leave as bottoms. The C₂ components leaving the top of the deethanizer are fed to an acetylene converter and then to a C₂ splitter which produces ethylene as the light product and ethane as the heavy product. The C₃ to C₅⁺ stream leaving the bottom of the deethanizer is routed to a depropanizer, which sends the C₃ components overhead and the C₄ to C₅⁺ components below. The C₃ product may be hydrotreated to remove C₃ acetylene and diene before being fed to a C₃ splitter, where it is separated into propylene at the top and propane at the bottom, while the C₄ to C₅⁺ stream is fed to a debutanizer, which produces C₄ components at the top with the balance of C₅⁺ components leaving as bottoms to be used for gasoline or to be recirculated into the pyrolysis furnace or cracker as feedstock. Both the C₄ and the C₅⁺ streams may be separately hydrotreated to remove undesirable acetylenes and dienes.

In conventional front-end deethanizer sequences, the quenched and acid free gases containing C₁ to C₅⁺ components first enter a deethanizer. The light ends exiting the deethanizer consist of C₂ and C₁ components along with any hydrogen. These light ends are fed to a demethanizer where the hydrogen and C₁ are removed as light ends and the C₂ components are removed as heavy ends. The C₂ stream leaving the bottom of the demethanizer is fed to an acetylene converter and then to a C₂ splitter which produces ethylene as the light product and ethane as the heavy product. The heavy ends exiting the deethanizer which consist of C₃ to C₅⁺ components are routed to a depropanizer which sends the C₃ components overhead and the C₄ to C₅⁺

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components below. The C₃ product is fed to a C₃ splitter where it is separated into propylene at the top and propane at the bottom, while the C₄ to C₅⁺ stream is fed to a debutanizer which produces C₄ compounds at the top with the balance leaving as bottoms to be
5 used for gasoline or to be recirculated. As with the front-end demethanizer sequence, the C₃, C₄, and C₅⁺ streams may separately hydrotreated to remove undesirable acetylenes and dienes.

10 In conventional front-end depropanizer sequences, the quenched and acid-free gases containing hydrocarbons having from one to five or more carbon atoms per molecule (C₁ to C₅⁺) first enter a depropanizer. The heavy ends exiting the depropanizer consist of C₄ to C₅⁺ components. These are routed
15 to a debutanizer where the C₄'s and lighter species are taken over the top with the rest of the feed leaving as bottoms which can be used for gasoline or other chemical recovery. These streams may be separately hydrotreated to remove undesired acetylenes and dienes. The tops of the depropanizer, containing C₁ to C₃
20 components, are fed to an acetylene converter and then to a demethanizer system, where the C₁ components and any remaining hydrogen are removed as an overhead. The heavy ends exiting the demethanizer system, which contains C₂ and C₃ components, are introduced into a deethanizer wherein C₂
25 components are taken off the top and C₃ compounds are taken from the bottom. The C₂ components are, in turn, fed to a C₂ splitter which produces ethylene as the light product and ethane as the heavy product. The C₃ stream is fed to a C₃ splitter which separates the C₃ species, sending propylene to the top and
30 propane to the bottom.

In conventional distillation sequences, as described above, multiple hydrogenation units are used to remove contaminants.

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The location and complexity of a typical hydrogenation unit is set by the compatibility of process conditions with the hydrogenation catalyst system used and the products being treated. Hydrogenation units required for the production of the
5 aforementioned marketable distillation products include, in addition to the acetylene converter which treats the C₂ stream, a methylacetylene/ propadiene converter ahead of the C₃ splitter to remove contaminants from propylene and propane products and to avoid the build-up of methylacetylene and propadiene in the C₃
10 splitter, a hydrogenation unit ahead of the debutanizer to remove C₄ and C₅ acetylenes from C₄ and C₅ olefins, and either a heat soaker or a hydrogenation unit on the debutanizer bottoms to remove additional C₅ acetylenes from pyrolysis gasoline. There is, therefore, a requirement of multiple, separate and distinct
15 hydrogenation units. While such a configuration is generally effective to remove contaminants such as methylacetylene, propadiene, C₄, and C₅ acetylene, it is complex and costly. The hydrogenation units required in this configuration are often very similar in nature and often require large recycle loops to moderate
20 the reaction and fractionation facilities to remove excess hydrogen and other gases. Furthermore, since the hydrogenation units are downstream of most the equipment in a steam cracker facility, the equipment, such as fractionators, boilers and pumps, is often subject to costly fouling due to the presence of undesired
25 contaminants.

It is therefore desirable to provide a treatment method for fractionating the C₂, C₃ and C₄ hydrocarbon components from a steam cracked hydrocarbon stream, e.g., a steam cracked
30 hydrocarbon stream, which eliminates or reduces fouling in the fractionation units caused by di-olefinically, poly-olefinically, and acetylenically unsaturated hydrocarbon contaminants in the stream

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without unduly complicating the process sequence or increasing the capital and processing costs of the operation.

SUMMARY OF THE INVENTION

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According to the invention there is provided a process for selectively hydrogenating di-olefinically, poly-olefinically and acetylenically unsaturated hydrocarbon components in a cracked hydrocarbon stream comprising the steps of:

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(a) feeding to a first separation unit a feedstock comprising a C₂ to C₅⁺ fraction of the cracked hydrocarbon stream;

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(b) removing from the first separation unit a heavy stream enriched in at least a C₄ to C₅⁺ fraction;

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(c) reacting the heavy stream with hydrogen under conditions to selectively hydrogenate di-olefinically, poly-olefinically and acetylenically unsaturated hydrocarbon components to form a hydrogenated stream;

(d) returning at least a portion of the hydrogenated stream to the first separation unit.

In a second embodiment, removing of the heavy stream is by means of a side draw. While in a third embodiment, removing of the heavy stream is by means of a reboiler circuit.

In any of the preceding embodiments, the first separation unit may be a deethanizer. In the preceding embodiments, the cracked hydrocarbon stream may be fed to a demethanizer upstream of the first separation unit and fractionated into a light stream and a demethanized stream and the demethanized stream which is the feedstock for the first separation unit. In another

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preferred embodiment, a portion of the hydrogenated stream is fed to a depropanizer located downstream of the first separation unit to separate a C₃ fraction from the C₄ to C₅⁺ fraction.

5 In still another embodiment, the first separation unit is a depropanizer for separating hydrogen and a C₁ to C₃ fraction from the C₄ to C₅⁺ fraction. In a preferred embodiment, the step of separating the hydrogen and C₁ to C₃ fraction into individual hydrogen rich, C₁ hydrocarbon, C₂ hydrocarbon and C₃
10 hydrocarbon component streams is added.

In another embodiment, the process of any of the preceding embodiments, further comprises the step of feeding at least a portion of the hydrogenated stream to a second separation unit to
15 split the C₄ species from the C₅⁺ species.

In yet another embodiment, the excess hydrogen is removed from the hydrogenated stream. In a preferred embodiment, the hydrogen is removed by passing the hydrogenated stream into
20 contact with a nonselective reactive catalyst bed.

This invention comprises novel processing sequences for treating a cracked hydrocarbon stream which result in the reduction of the quantity of di-olefinically, poly-olefinically and
25 acetylenically unsaturated hydrocarbon contaminants therein which are primarily responsible for fouling of equipment. More specifically, the invention relates to the placement of a hydrogenation unit on a first separation unit of the processing sequence. The first separation unit in such described sequence
30 may be either a deethanizer or a depropanizer. However, a demethanizer may optionally be placed upstream of such first separation unit, for treatment of the feedstock to the first unit. The hydrogenation unit may be placed to operate on either a side draw

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or on the bottoms of the first separation unit. The use of upstream hydrogenation according to the invention is applicable to front-end demethanizer, front-end deethanizer or front-end depropanizer processing sequences.

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As a further advantage, application of this invention enables the simplification of the processing equipment requirements for units downstream from the first separation unit. Thus, the need to separately submit to hydrogenation the effluent stream products from the various fractionation towers may be overcome, thereby eliminating the need for multiple hydrogenation units in the overall processing sequence.

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The novel flow sequences of the invention mean that fouling may be reduced or prevented by replacing the conventional multiple hydrogenation unit configuration of fractional distillation flow sequences with an upstream hydrogenation unit configuration which preferably operates in conjunction with an acetylene converter.

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The upstream hydrogenation unit configuration of the process of the invention uses a hydrogenation unit located on either a side draw or in the reboiler circuit of a deethanizer or depropanizer in a front-end demethanizer, front-end deethanizer or a front-end depropanizer sequence for the recovery of various olefin products via fractional distillation of a cracked hydrocarbon stream.

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BRIEF DESCRIPTION OF THE DRAWINGS

The above and other embodiments of the present invention may be more fully understood from the following detailed description, when taken together with accompanying drawings wherein similar reference characters refer to similar elements throughout, and in which:

Figure 1 is a flow diagram of a portion of the process for the separation of cracked hydrocarbons of the present invention featuring, in Figure 1A, a hydrogenation unit operating on a side liquid draw, and in Figure 1B, a hydrogenation unit operating in a reboiler circuit.

Figure 2 is a flow diagram of a conventional front-end demethanizer process for the separation of cracked hydrocarbons.

Figure 3 is a flow diagram of a conventional front-end deethanizer process for the separation of cracked hydrocarbons.

Figure 4 is a flow diagram of a conventional front-end depropanizer process for the separation of cracked hydrocarbons.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention comprises processing sequences for the reduction of fouling in the treatment of a cracked hydrocarbon stream, involving the use of an upstream hydrogenation unit, preferably in conjunction with an acetylene converter, rather than the conventional multiple hydrogenation unit configurations.

In Figure 1A, a feedstock 40 which may consist of a quenched, acid-free hydrocarbon stream containing either a full C₁

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to C₅⁺ component stream or a C₂ to C₅⁺ stream (if the stream has first been subjected to separation in a demethanizer), is fed to a first separation unit 41. The feedstock 40 is fractionated in the first separation unit 41 into a tops stream 42 and a bottoms stream 48.

5 At an intermediate step in the fractionation, a collection tray 43 collects components in a liquid phase. These liquid components are removed from the first separation unit 41 through a side liquid draw 44 and are fed to a hydrogenation unit 45 wherein the side liquid draw 44 material is reacted with hydrogen 46 under

10 conditions of temperature, pressure and over a catalyst selective for the hydrogenation of the di-olefinic, poly-olefinic and acetylenic contaminants contained therein. The source of hydrogen 46 may be for example from a high purity hydrogen source or from tail gas obtained from the pyrolysis effluent which contains sufficient levels

15 of hydrogen for efficient hydrogenation to take place, thereby eliminating the expense associated with the high purity hydrogen source.

The heavy components and oligomers which result from

20 hydrogenation of the aforementioned contaminants and which have not been converted to olefins are commonly referred to as "green oil." The "green oil" components are non-fouling with regard to their passage through subsequent processing units. Following the hydrogenation, the so-hydrogenated stream leaving the

25 hydrogenation unit 45 may optionally be treated to remove excess hydrogen by first contacting it with a nonselective reactive catalyst bed (not illustrated).

The so-hydrogenated stream 47 is fed back to the first

30 separation unit where the stream is further fractionated and the heavy fraction, which has been hydrogenated, leaves as bottoms 48. The bottoms stream 48 may be further treated in a depropanizer (not illustrated) to separate the C₃ compounds from

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the C₄ and C₅⁺ compounds, depending upon which sequence is being utilized. In any event, the bottoms streams 48 is eventually, in a preferred embodiment of the invention, fed to a second unit (not illustrated) which serves as a debutanizer to separate the C₄ compounds from the C₅⁺ compounds.

In the above described embodiment of the invention, the hydrogenation unit may be located at a side liquid draw of either a deethanizer, in a front-end demethanizer sequence or front-end deethanizer sequence, or a depropanizer, in a front-end depropanizer sequence. Alternatively, the side draw may be of a gaseous phase or may be of a mixed phase.

Placing the hydrogenation unit at the side liquid draw is advantageous in comparison to the use of multiple hydrogenation units downstream because the contaminants are removed prior to getting to the high temperature zone of the first separation unit. As a result, the hydrogenation unit at this location reduces fouling both in the first separation unit and in its accompanying reboiler circuit. Additionally, another benefit of this location is that the need for a recycle stream, which is typically required to insure that the concentration of contaminants into the hydrogenation unit be of sufficiently low concentration, may be eliminated as the reboiler circuit rate can be adjusted to serve this purpose.

Still another benefit of the side draw location is that the excess hydrogen required to operate the hydrogenation unit goes to the first separation unit where it is removed overhead. This eliminates the need for separate hydrogen removal facilities which are required for the multiple hydrogenation unit configurations.

An alternative embodiment is depicted in Figure 1B in which a feedstock 40 which may consist of a quenched, acid free

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hydrocarbon stream containing either a full complement of C₁ to C₅⁺ components or a C₂ to C₅⁺ stream (in the case where a front-end demethanizer is used), is fed to a first separation unit 41.

5 The feedstock 40 is routed to a first separation unit 41 where a top stream 42 is separated from a bottom stream 48. The heavy stream 48 leaving the bottom of the first separation unit 41 in addition to containing desirable product components such as isobutylene, butadiene, amylene and pyrolytic gasoline, also
10 contains as undesirable contaminants, which produce fouling of the downstream units, di-olefinic, poly-olefinic and acetylenic compounds such as methylacetylene and propadiene.

 In accordance with this embodiment of the present
15 invention, the heavy stream 48 leaving the bottom of the first separation unit 41 is fed to a hydrogenation unit 45 wherein the heavy stream 48 is reacted with hydrogen 46 under conditions of temperature, pressure and over a catalyst selective for the hydrogenation of the di-olefinic, poly-olefinic and acetylenic
20 contaminants contained therein. The source of hydrogen 46 may be, for example, from a high purity hydrogen source, or from tail gas obtained from the pyrolysis effluent which contains sufficient levels of hydrogen for efficient hydrogenation to take place, thereby eliminating the expense associated with the high purity
25 hydrogen source. The heavy components and oligomers which result from hydrogenation of such contaminants and which have not been converted to olefins are commonly referred to as "green oil." The "green oil" components are non-fouling with regards to their passage through subsequent processing units. Following the
30 hydrogenation reaction, the so hydrogenated stream 47 leaving the hydrogenation unit 45 may be treated to remove excess hydrogen by first contacting it with a nonselective reactive catalyst bed (not illustrated) and this product or the hydrogenated product stream

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may be split into a first and second portion 50 and 49. The first portion of the hydrogenated product stream 50 is fed to reboiler 51 and is heated to a temperature of from about 50° to about 150°C at a pressure of from about 1000 to about 3000 kPa and then
5 returned by line 52 to the bottom of the first separation unit 41.

The bottoms stream 49 may be further treated in a depropanizer (not illustrated) to separate the C₃ compounds from the C₄ and C₅ compounds, depending upon which sequence is
10 being utilized. In any event, the bottoms stream 49 is eventually preferably fed to a second unit (not illustrated) which serves as a debutanizer to separate the C₄ compounds from the C₅⁺ compounds.

15 In the above described embodiment, the hydrogenation unit may be located in the reboiler circuit of either a deethanizer (in a front-end demethanizer sequence or a front-end deethanizer sequence) or a depropanizer (in a front-end depropanizer sequence). Placing the hydrogenation unit in one of the above
20 referenced locations is advantageous in comparison to the use of multiple hydrogenation units downstream because it optimizes the defouling performance of the hydrogenation unit since the bulk of the fouling contaminants are concentrated in the reboiler circuit. Additionally, location of the hydrogenation unit at this location
25 reduces fouling in the reboiler circuit of the first separation unit. Yet another benefit of this location is that the need for the standard hydrogenation feed pump, which is employed to insure that the feed to the hydrogenation unit is in liquid form is eliminated. The recycle stream, which is typically required to insure that the
30 concentration of contaminants into the hydrogenation unit be sufficiently low, may be eliminated as the reboiler circuit rate can be adjusted to serve this purpose.

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The alternative embodiments depicted in Figures 1A and 1B may be employed in conjunction with a variety of alternative sequences, namely front-end demethanizer, front-end deethanizer or front-end depropanizer sequences. The optional location of the hydrogenation unit in a side draw or reboiler unit, ultimately depend upon the particular sequence employed and the given set of operating conditions.

Figures 2, 3 and 4 depict a front-end demethanizer sequence, a front-end deethanizer sequence and a front-end depropanizer sequence respectively. In any of these sequences feedstock 10 consisting of hydrocarbons, such as ethane, propane, butane, naphtha, or gas oil or mixtures thereof is introduced into a pyrolysis furnace 11 where feedstock 10 is pyrolyzed to form a mixture of products. The pyrolyzed gases 12 leaving the pyrolysis furnace 11 are quenched in a quench vessel 13 to arrest undesirable secondary reactions which tend to destroy light olefins. The quenched gases 14 are then compressed in a compressor 15. The compressed gases are fed to an acid gas removal vessel 16 where they undergo acid gas removal, typically with the addition of a base such as NaOH 17. At this point, the gas 18 contains hydrogen and hydrocarbons having from one to five or more carbon atoms per molecule (C_1 to C_5^+) and the aforementioned sequences diverge.

In the case of a front-demethanizer sequence as depicted in Figure 2, the gas 18 is fed to a demethanizer 19 wherein the C_1 fraction containing methane and any hydrogen 20 is removed. The bottoms stream 21 exiting the demethanizer 19 consists of the C_2 to C_5^+ species. These are routed to a deethanizer 22 where the light stream 23 containing C_2 components is taken over the top and the heavy stream 24 containing C_3 to C_5^+ components leaves out the bottom. The deethanizer 22 may be configured as the first

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separation unit 41 is depicted in either embodiment of Figure 1. The deethanizer 22 may therefore have a side liquid draw 44 which is fed to a hydrogenation unit 45 or alternatively the heavy stream 24 exiting as bottoms from the deethanizer 22 may be fed to a hydrogenation unit 45 in the reboiler circuit of the deethanizer 22. The light stream 23 leaving the deethanizer 22 is fed to an acetylene converter 25, and then is fed to a C₂ splitter or fractionator 26 which produces ethylene 27 as the light product and ethane 28 as the heavy product. The C₃ to C₅⁺ stream 24 leaving the bottom of the deethanizer 22 is fed into a depropanizer 29 which sends the light stream 30 containing the C₃ components overhead and the C₄ to C₅⁺ species 31 below. The light stream 30 may be fed into a splitter 32 to separate the C₃ stream into propylene 33 at the top and propane 34 at the bottom, while the C₄ to C₅⁺ stream 31 is fed to a debutanizer 35, the second unit referenced but not illustrated in the discussion of either embodiment of Figure 1, which produces the C₄ species at the top 36 with the C₅⁺ species leaving as bottoms 37 to be used as pyrolytic gasoline or recirculated into the pyrolysis furnace.

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In the case of a front-end deethanizer sequence, as depicted in Figure 3, the gas 18 is fed to a deethanizer 22 where the light stream 23 containing hydrogen, C₁ and C₂ components is taken over the top and the heavy stream 24 containing C₃ to C₅⁺ components leaves out the bottom. The deethanizer 22 may be configured as the first separation unit 41 is depicted in either embodiment of Figure 1. The deethanizer 22 may therefore have a side liquid draw 44 which is fed to a hydrogenation unit 45 or alternatively the heavy stream 24 exiting as bottoms from the deethanizer 22 may be fed to a hydrogenation unit 45 in the reboiler circuit of the deethanizer 22. The light stream 23 leaving the deethanizer 22 is fed to a demethanizer 19 where the C₁ fraction containing methane and any hydrogen 20 is removed. The

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bottoms stream 21 is fed to an acetylene converter 25, and then is fed to a C₂ splitter or fractionator 26 which produces ethylene 27 as the light product and ethane 28 as the heavy product. The heavy stream 24 exiting as bottoms from the deethanizer 22 is fed into a depropanizer 29 which sends the light stream 30 containing the C₃ components overhead and the C₄ to C₅⁺ species 31 below. The light stream 30 may be fed into a splitter 32 to separate the C₃ stream into propylene 33 at the top and propane 34 at the bottom, while the C₄ to C₅⁺ stream 31 is fed to a debutanizer 35, the second unit referenced but not illustrated in the discussion of either embodiment of Figure 1, which produces the C₄ species of the top 36 with the C₅⁺ species leaving as bottoms 37 to be used as pyrolytic gasoline or recirculated into the pyrolysis furnace.

In the case of a front-end depropanizer sequence, as depicted in Figure 4, the gas 18 is fed to a depropanizer 29 where the light stream 30 containing hydrogen and the C₁ to C₃ components leaves overhead and the C₄ to C₅⁺ species 31 exit below. The depropanizer 29 may be configured as the first separation unit 41 is depicted in either embodiment of Figure 1. The depropanizer 29 may therefore have a side liquid draw 44 which is fed to a hydrogenation unit 45 or alternatively the C₄ to C₅⁺ species 31 exiting as bottoms from the depropanizer may be fed a hydrogenation unit 45 in the reboiler circuit of the depropanizer 29. The light stream 30 leaving the depropanizer 29 is fed to an acetylene converter 25, and then is fed to a demethanizer 19 wherein the C₁ fraction containing methane and any hydrogen 20 is removed. The bottom stream 21 exiting the demethanizer 19 consists of the C₂ to C₃ species. These are routed to a deethanizer 22 where the light stream 23 containing C₂ components is taken over the top and the heavy stream 24 containing the C₃ species leaves out the bottom. The light stream 23 may be fed to a C₂ splitter or fractionator 26 which produces

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ethylene 27 as the light product and ethane 28 as the heavy product. The heavy stream 24 may be fed into splitter 32 to separate the C₃ stream into propylene 33 at the top and propane 34 at the bottom.

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The C₄ to C₅⁺ species 31 exiting the depropanizer 29 is fed to a debutanizer 35, the second unit referenced but not illustrated in the discussion of either embodiment of Figure 1, which produced the C₄ species at the top 36 with the C₅⁺ species leaving as bottoms 37 to be used as pyrolytic gasoline or recirculated into the pyrolysis furnace.

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As discussed above, the hydrogenation unit of the invention may be placed at either a side draw or in the reboiler circuit of either a deethanizer or a depropanizer. These locations reduce fouling of the hydrogenation unit and the towers and many of the subsequent, conventionally used hydrogenation units.

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In the case of the embodiment wherein the hydrogenation unit is used in association with a deethanizer, the two sequences which represent embodiments of the invention are the front-end demethanizer sequence and the front-end deethanizer sequence. Location of the hydrogenation unit upstream of the demethanizer, in the front-end demethanizer sequence, is not practical due to the low temperature of operation of that column and the restricted temperature ranges at which available hydrogenation catalysts operate, generally from about 5° to about 50°C. Location upstream of either the deethanizer or depropanizer, in the front-end deethanizer sequence or front-end depropanizer sequence respectively, is not practical since present hydrogenation conditions which optimize conversion of C₂ contaminants would affect the yield of heavier olefins, such as, for example, conversion of propylene to propane. It is preferred, therefore, that the

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feedstock which is hydrogenated in the hydrogenation unit of the invention consist primarily of C₃, C₄, and C₅⁺ species or component species thereof.

5 In the case of the embodiment wherein hydrogenation takes place in association with a deethanizer, that hydrogenation unit will be fed a mixture C₃ to C₅⁺ species. In the case of the embodiment wherein the hydrogenation takes place in association with a depropanizer, that hydrogenation unit will be fed a mixture of
10 C₃ to C₅⁺ primarily species where the feed is from the side draw or a mixture of C₄ to C₅⁺ species where the feed is in the reboiler circuit.

 Given the narrow temperature range over which the desired
15 hydrogenation will occur and undesired reactions are minimized, heat liberated during the hydrogenation is often enough to exceed the temperature range so the hydrogenation unit may require a recycle of product to dilute the reacting components and thus moderate the rise in temperature. Such a recycle may be easily
20 accommodated by the reboiler circuit. Some of the heat generated by the reaction may be used to aid in the reboiling.

 The preferred catalysts used in the hydrogenation unit are supported catalysts. The supports may be standard, inert supports
25 such as alumina or silica. The active ingredient of the catalyst used in the hydrogenation unit of the invention consists of, for example, palladium. In a preferred embodiment, enhancers are used to optimize operation of the hydrogenation unit. Such enhancers include gold, silver, vanadium and the like. These
30 catalysts may also be used as the catalyst in the above referenced nonselective catalyst bed.

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EXAMPLES

To illustrate the advantage of one embodiment of the invention over the prior art, a computer simulation was run as an example. This case is for the depropanizer first sequence. Case I illustrates the prior art as a comparative example and Case II illustrates one of the embodiments in which a side liquid draw on the depropanizer is utilized. Both cases have equivalent fouling rates as measured by tower run length.

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**CASE I.
COMPARATIVE**

Component Flow Rate, Kg/Hr	Depropanizer		
	Feed	Overhead	Bottoms
C2's and lighter	143,356	143,356	0
Propane	5,414	5,414	0
Propylene	26,493	26,493	0
Methylacetylene & Propadiene	1,363	1,354	9
C4 Paraffins	3,017	4	3,012
C4 Olefins	2,995	0.45	2,954
Butadiene	8,058	0.45	8,057
C4 Acetylenes	785	0	785
C5's and heavier	15,168	0	15,168
Total	206,649	176,621	29,685
Temperature, C°		-40	71
Pressure, kPa		1,030	

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**CASE II.
ACCORDING TO INVENTION**

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Component Flow Rate, Kg/hr	Depropanizer		
	Feed	Overhead	Bottoms
C2's and lighter	143,356	143,440	0
Propane	5,414	5,412	3
Propylene	26,493	27,417	.45
Methylacetylene & Propadiene	1,363	526	7
C4 Paraffins	3,017	0	3,017
C4 Olefins	2,955	0	3,971
Butadiene	8,058	0	7,687
C4 Acetylenes	785	0	99
C5's and heavier	15,168	0	15,168
Total	206,649	176,795	29,952
Temp, C°		-41	107
Pressure, kPa		1,030	

One can see from the data that one can operate at a higher temperature (107°C) with this embodiment vs. the comparative example (71°C) which results in equivalent fouling or the same tower run length. One can further observe the reduction of methyl acetylene and propadiene in the tower overhead from 1,354 kg/hr to 526 kg/hr. Similarly the C₄ acetylenes in the bottoms are reduced from 785 kg/hr to 99 kg/hr through the practice of one embodiment of the invention. In an operating facility one could alternatively choose to operate at lower temperature conditions and achieve a much longer tower run length.

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Benefits are also seen in the downstream debutanizer. In Case I, the debutanizer runs at 70 kPa, while for Case II, the debutanizer runs at 255 kPa (and therefore higher temperatures) with an equivalent fouling rate.

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In the foregoing example the methylacetylene plus propadiene concentration in the feed is 1,363 / 279,446 or 0.48%. Those skilled in the art will recognize that this concentration will vary, typically from about 0.4% up to about 1.4% depending on the operating conditions in the pyrolysis furnaces and the feedstock selected. Similarly, the C₄ acetylene concentration in the feed is 785 / 279,146 or 0.28%. Those skilled in the art will likewise recognize that this concentration will vary, typically from about 0.04% up to about 2.5% also depending on the operating conditions in the pyrolysis furnace and the feedstock selected. Although the concentration of contaminants such as methylacetylene, propadiene, and C₄ acetylenes can vary, for example through the ranges mentioned, the results achieved by performance of the invention are typified by that described in the foregoing example.

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CLAIMS:

1. A process for selectively hydrogenating di-olefinically, poly-olefinically and acetylenically unsaturated hydrocarbon components in a cracked hydrocarbon stream comprising the steps of:
- 5 (a) feeding to a first separation unit a feedstock comprising a C₂ to C₅⁺ fraction of the cracked hydrocarbon stream;
- 10 (b) removing from the first separation unit a heavy stream enriched in at least a C₄ to C₅⁺ fraction;
- 15 (c) reacting the heavy stream with hydrogen under conditions to selectively hydrogenate di-olefinically, poly-olefinically and acetylenically unsaturated hydrocarbon components to form a hydrogenated stream;
- 20 (d) returning at least a portion of the hydrogenated stream to the first separation unit.
2. The process of Claim 1, wherein the removing of the heavy stream is by means of a side draw.
3. The process of Claim 1, wherein the removing of the heavy stream is by means of a reboiler circuit.
- 25 4. The process of any preceding claims, wherein the first separation unit is a deethanizer.
- 30 5. The process of Claim 4, wherein the cracked hydrocarbon stream is fed to a demethanizer upstream of the first separation unit and fractionated into a light stream and a



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demethanized stream and the demethanized stream which is the feedstock for the first separation unit.

- 5 6. The process of Claim 4 or 5, wherein a portion of the hydrogenated stream is fed to a depropanizer located downstream of the first separation unit to separate a C₃ fraction from the C₄ to C₅⁺ fraction.
- 10 7. The process of Claim 1, 2, or 3, wherein the first separation unit is a depropanizer for separating hydrogen and a C₁ to C₃ fraction from the C₄ to C₅⁺ fraction.
- 15 8. The process of claim 7 further comprising the step of separating the hydrogen and C₁ to C₃ fraction into individual hydrogen rich, C₁ hydrocarbon, C₂ hydrocarbon and C₃ hydrocarbon component streams.
- 20 9. The process of any of the preceding claims, further comprising the step of:
 - (e) feeding at least a portion of the hydrogenated stream to a second separation unit to split the C₄ species from the C₅⁺ species.
- 25 10. The process of any of the preceding claims, further comprising the step of removing excess hydrogen from the hydrogenated stream.
- 30 11. The process of Claim 10, wherein the hydrogen is removed by passing the hydrogenated stream into contact with a nonselective reactive catalyst bed.



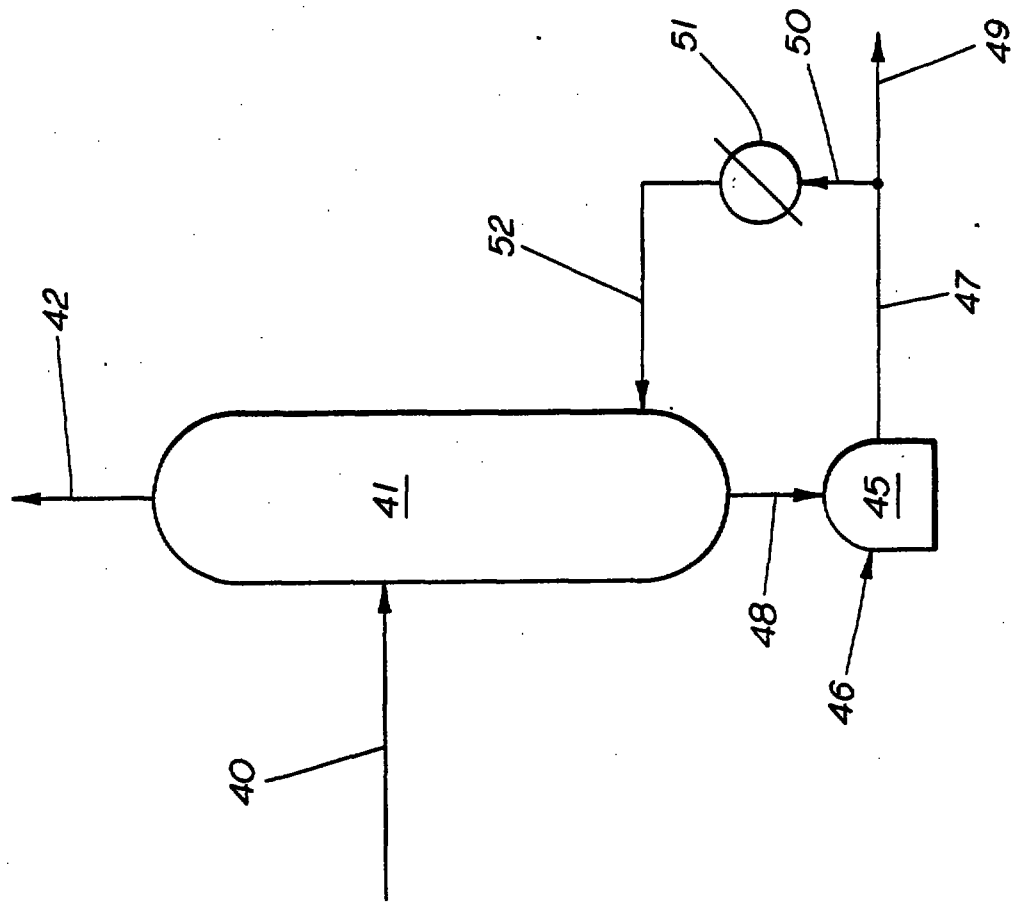


FIG.1B

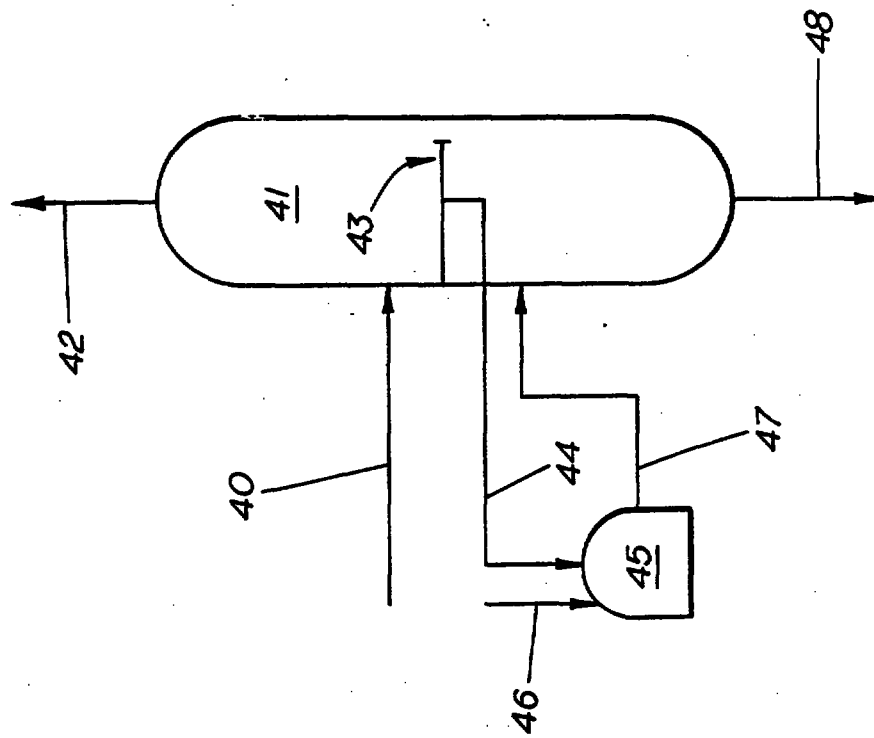


FIG.1A

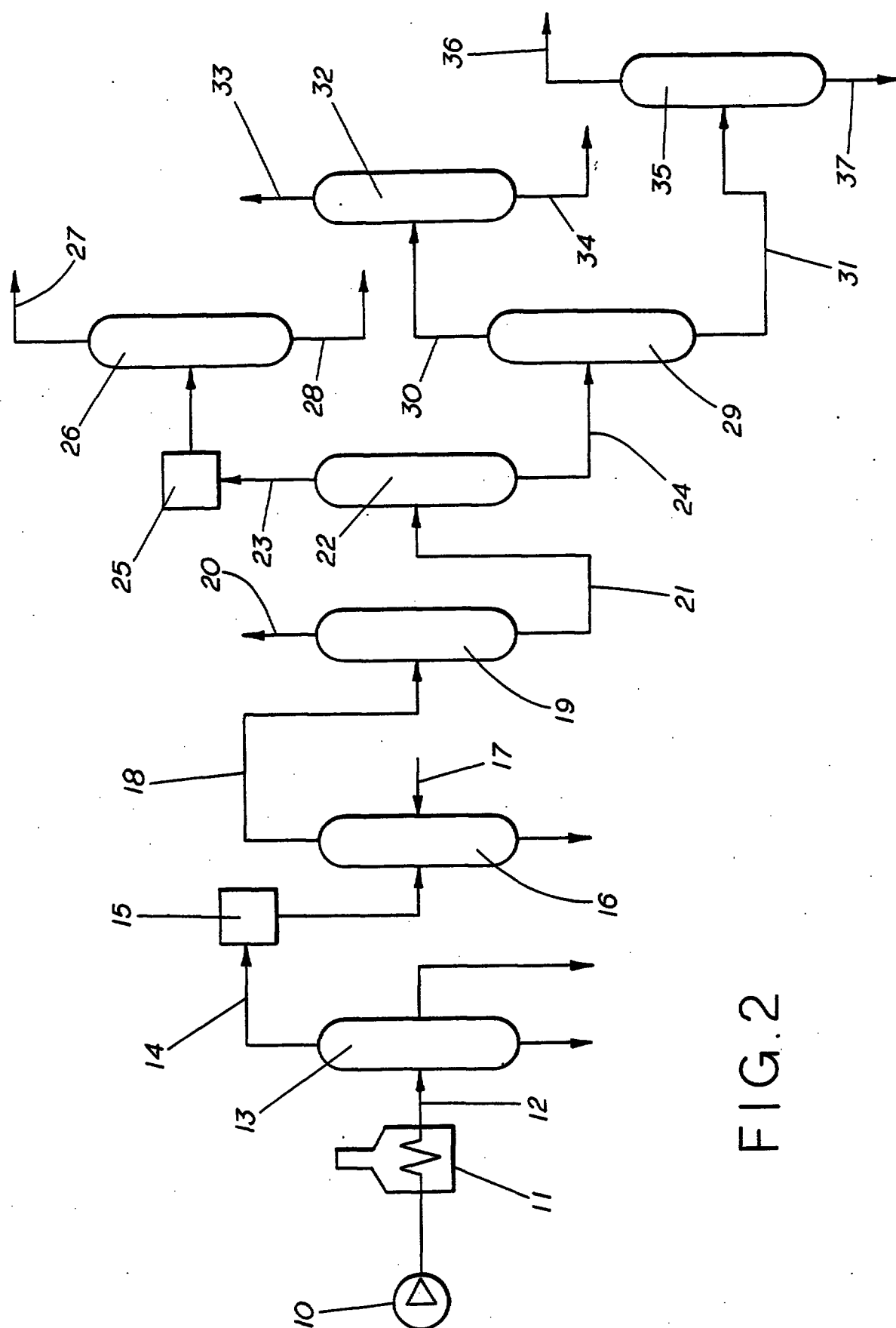


FIG. 2

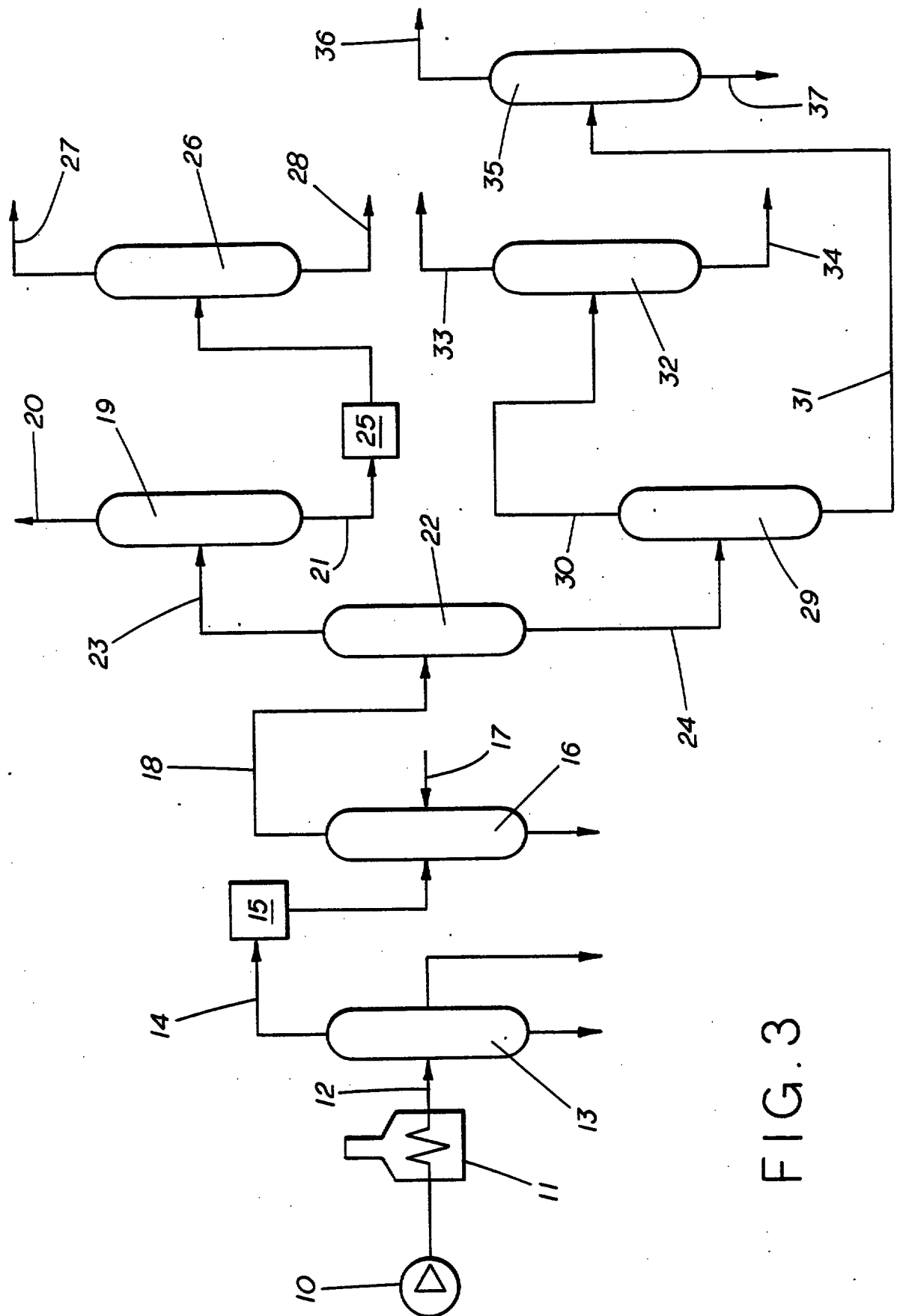


FIG. 3

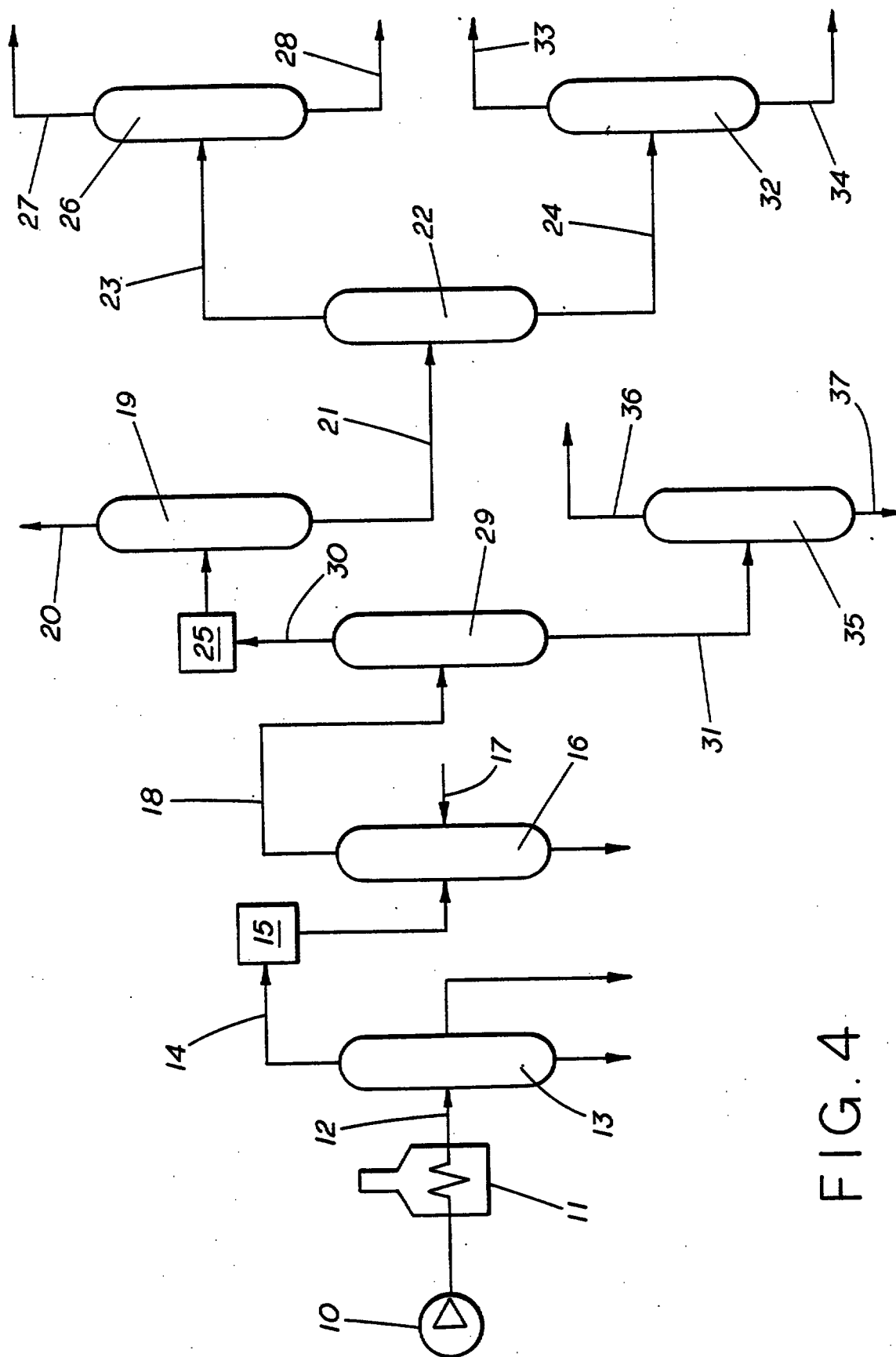


FIG. 4



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(21) International Application Number: PCT/US95/11000 (22) International Filing Date: 25 August 1995 (25.08.95) (30) Priority Data: 08/296,767 ✓ 26 August 1994 (26.08.94) ✓ US (71) Applicant: EXXON CHEMICAL PATENTS INC. [US/US]; 5200 Bayway Drive; Baytown, TX 77520 (US). ✓ (72) Inventors: VEBELIUNAS, Rimas, Virgilijus; 8318 Cedarbrake, Houston, TX 77055 (US). BAMPFORD, David, Alan; 5615 Wigton Drive, Houston, TX 77096 (US). DRUMMOND, Neil, James; 16 Liggars Place, Dunfermline, Fife KY12 7XZ (GB). SNIDER, Sheri, Renee; 518 Columbia, Houston, TX 77007 (US). STRACK, Robert, David; 1906 Park Lodge Court, Houston, TX 77062 (US). HALLE, Roy, Thomas; 912 Davis Road, League City, TX 77573 (US). (74) Agents: ZBORAY, James, A.; Exxon Chemical Company, P.O. Box 2149, Baytown, TX 77522-2149 (US) et al.	(81) Designated States: AU, CA, JP, SG, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(54) Title: PROCESS FOR SELECTIVE HYDROGENATION OF CRACKED HYDROCARBONS		
(57) Abstract		
The invention relates to a process to selectively hydrogenate di-olefinically, poly-olefinically, and acetylenically unsaturated hydrocarbon components a C₂ to C₅⁺ or a C₃ to C₅⁺ fraction of a cracked hydrocarbon stream. The process comprises removing from a deethanizer or depropanizer a heavy stream enriched in a C₃ to C₅⁺ or a C₄ to C₅⁺ fraction; reacting the heavy stream with hydrogen for selective hydrogenation; and returning at least a portion of the hydrogenated stream to the deethanizer or depropanizer. Embodiments are disclosed where the heavy stream is removed by a side draw or by means of the reboiler circuit. The invention is applicable to front-end demethanizer, deethanizer, or depropanizer fractional distillation process sequences such as may be used with steam cracking or catalytic cracking.		

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