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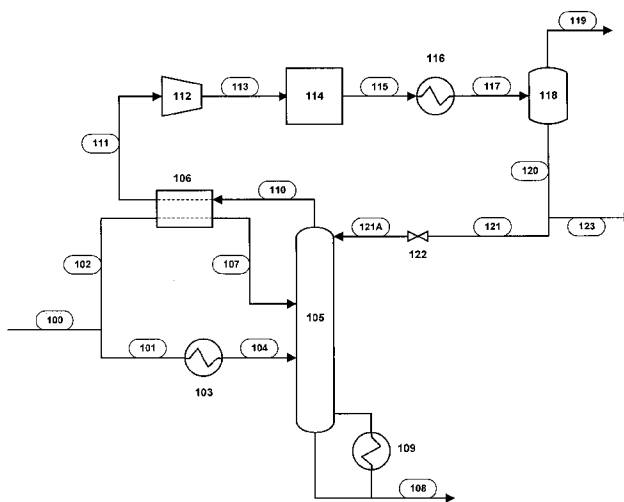
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(54) Title: CRYOGENIC FRACTIONATION PROCESS



(57) Abstract: Processes using cryogenic distillation columns in a front-end fractionation unit that more efficiently recover one or more useful component from a mixture containing a plurality of volatile organic compounds are disclosed. Beneficially, processes of the invention are used for initial fractionation of cracked gas stream (100) containing olefins such as are typically produced by thermal cracking of suitable hydrocarbon feedstocks, by chilling a portion of the cracked gas stream by indirect heat exchange (106) with the column overheads stream (110), directing the chilled portion to the cryogenic distillation tower (105), and directing a second portion (101) of the cracked gas stream to separate point on the cryogenic distillation tower.



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## CRYOGENIC FRACTIONATION PROCESS

### STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

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### FIELD OF THE INVENTION

The field of this invention relates to use of a cryogenic distillation column in a fractionation unit to more efficiently recover one or more useful component from a mixture containing a plurality of volatile organic compounds. Processes according to this invention are particularly useful for at least partial separation of components from a mixed gas stream in an olefins manufacturing process. Beneficially, processes of the invention are used for initial fractionation of cracked gas stream containing olefins. Such streams are typically produced by thermal or catalytic cracking of suitable petroleum derived feedstocks, and the olefins being recovered and purified are typically ethylene and/or propylene.

### BACKGROUND OF THE INVENTION

As is well known, olefins, or alkenes, are a homologous series of hydrocarbon compounds characterized by having a double bond of four shared electrons between two carbon atoms. The simplest member of the series, ethylene, is the largest volume organic chemical produced today. Olefins including, importantly, ethylene, propylene and smaller amounts of butadiene, are converted to a multitude of intermediate and end products on a large scale, mainly polymeric materials.

Commercial production of olefins is almost exclusively accomplished by pyrolysis of hydrocarbons in tubular reactor coils installed in externally fired heaters. Thermal cracking feed stocks include streams of ethane, propane or hydrocarbon liquids ranging in boiling point from light straight-run gasoline through gas oil.

In a typical ethylene plant the cracking represent about 25 percent of the cost of the unit while the compression, heating, dehydration, recovery and refrigeration sections represent the remaining about 75 percent of the total. This endothermic process is carried out in large pyrolysis furnaces with the expenditure of large quantities of heat which is provided in part by burning the methane produced in the cracking process. After cracking, the reactor effluent is put

through a series of separation steps involving cryogenic separation of products such as ethylene and propylene. The total energy requirements for the process are thus very large and ways to reduce it are of substantial commercial interest.

Several methods are known for separation of an organic gas containing unsaturated linkages from gaseous mixtures. These include, for instance, cryogenic distillation, liquid sorption, membrane separation and the so called "pressure swing adsorption" in which sorption occurs at a higher pressure than the pressure at which the sorbent is regenerated. Cryogenic distillation is a common technique for separating alkenes, such as ethylene, from gaseous mixtures containing molecules of similar size, e.g., ethane or methane. However, cryogenic techniques have disadvantages such as high capital cost and high operating expenses.

Listed below are the mole weight and atmospheric boiling points for the light products from thermal cracking and some common compounds potentially found in an olefins unit. Included are some compounds which have similar boiling temperatures to cracked products and may be present in feedstocks or produced in trace amounts during thermal cracking.

Mole Compound	Weight	Normal Boiling Point, °C
Hydrogen	2.016	-252.8
Nitrogen	28.013	-195.8
Carbon monoxide	28.010	-191.5
Oxygen	31.999	-183.0
Methane	16.043	-161.5
Ethylene	28.054	-103.8
Ethane	30.070	-88.7
Phosphine	33.970	-87.4
Acetylene *	26.038	-84.0
Carbon dioxide *	44.010	-78.5
Radon	222.00	-61.8
Hydrogen sulfide	34.080	-60.4
Arsine	77.910	-55.0
Carbonyl sulfide	60.070	-50.3
Propylene	42.081	-47.8
Propane	44.097	-42.1
Propadiene (PD)	40.065	-34.5
Cyclo-propane	42.081	-32.8
Methyl acetylene	40.065	-23.2
Water	18.015	100.

\*Sublimation temperature

Recently the trend in the hydrocarbon processing industry is to reduce commercially acceptable levels of impurities in major olefin product streams, i.e., ethylene, propylene, and hydrogen. The need for purity improvements is directly

related to the increasing use of higher activity catalysts for production of polyethylene and polypropylene, and to a limited extent other olefin derivatives.

U.S. Pat. No. 6,354,105 in the name of Rong-Jwyn Lee, Pallav Jain, Jame Yao, Jong Juh Chen and Douglas G. Elliot (Lee et al.) describes a split feed  
5 compression process for recovery of ethylene, ethane and heavier components using a cryogenic distillation column which involved dividing the feed gas into a first gaseous stream and a main gaseous stream. The first gaseous stream is compressed and cooled, and then expanded and introduced into the top of a cryogenic distillation column as a main reflux stream.

10 Lee et al. described a process specific to demethanizer towers, but did not address use of towers in which the ethane or ethylene is recovered to the overhead from the tower. Lee et al. state that a beneficial aspect of their process is high recovery of C2 hydrocarbons to the tower bottoms stream.

15 De Cintio et al (*Hydrocarbon Processing*, July 1991, pp 83-90) describe a front-end deethanizer tower which utilizes a two-feed arrangement, one vapor and one liquid feed. They did not disclose or suggest reducing energy requirements of the process by heat integrating tower overheads with feed chilling.

20 Ethylene separation and purification is typically done via cryogenic distillation. Many different process designs have been suggested for the separation and purification of ethylene from the cooled and compressed reactor effluent gas. A summary of such designs which are currently commercially available has been published recently (*Hydrocarbon Processing*, March 2003, pp 96-98).

25 These designs have typically been grouped in terms of the initial rectification operation that is performed. For example, in a "front end demethanizer" design the compressed, cooled cracked gas is directed to a demethanizer feed chilling train in which it is successively chilled and partially condensed. The condensed liquids are separated and directed to a demethanizer tower. In this tower the methane and lighter components are recovered into the  
30 demethanizer overhead stream and the ethylene and heavier components are recovered into the demethanizer bottoms stream. The ethylene and heavier components are typically sent to a deethanizer column where any components heavier than ethane are recovered into the deethanizer bottoms stream. The deethanizer overhead stream contains primarily ethylene, ethane and acetylene  
35 and is directed to an acetylene removal step, such as a hydrogenation reactor.

The essentially acetylene-free stream from the hydrogenation reactor is then directed to a C2 splitter column where the ethylene and ethane are separated. Front end demethanizer designs are often used when the ethylene is produced from a relatively heavy feedstock, such as a naphtha or gas oil.

5 "Front-end deethanizer" methods include those in which a deethanizer tower is the initial rectification operation that is performed. In these methods the cracked gas is chilled and directed to a deethanizer tower. The overhead of the deethanizer contains primarily methane, hydrogen, ethylene and ethane, while components heavier than ethane are recovered to the deethanizer bottoms Front-  
10 end deethanizer methods are often utilized when the steam cracker feed is a light gas such as ethane, propane, butane, or a mixture of these.

"Front-end depropanizer" methods are similar to front-end deethanizer methods, except that the first step is to remove the propane and lighter components from the cracked gas stream. In this case the depropanizer overhead  
15 stream contains propane and lighter components, while components heavier than propane are recovered to the depropanizer bottoms.

In general the optimal separation method will depend on many factors, including feed type, product requirements, energy cost, and feed cost, among others. However, all of these methods are cryogenic in nature, that is they operate  
20 at temperatures below ambient, and therefore require significant energy in the form of refrigeration power

It is therefore a general object of the present invention to provide an improved process which overcomes the aforesaid problem of prior art methods, for recovery and separation of desirable components from gaseous mixtures  
25 recovery, but does not require appreciable increases in capital and operating costs.

More particularly, it is an object of the present invention to provide an improved method for recovery and at least partial purification of ethylene and/or propylene from a cracked gas mixture.

30 An improved method for recovery of one or more useful components from mixtures containing a plurality of volatile organic compounds should exhibit higher efficiency thereby providing lower variable costs of operation.

Other objects and advantages of the invention will become apparent upon reading the following detailed description and appended claims.

## SUMMARY OF THE INVENTION

Economical processes are disclosed for recovery of one or more useful component from a mixture containing a plurality of volatile organic compounds, especially for cryogenically recovering components of a relatively impure olefins stream produced by thermal cracking of hydrocarbons. Processes of this invention comprise: providing a fractionation unit comprising a cryogenic distillation column having an overhead outlet and reflux inlet near the top of the column, two or more feed inlets below the reflux inlet, and an outlet for liquid residue from the bottom of the column; fractionating a mixture of organic compounds to thereby obtain at least an overhead stream comprising a portion of the more volatile components and a liquid residue comprising a portion of the less volatile components of the mixture; heating at least a portion of the overhead stream by indirect heat exchange with a first portion of the mixture, processing the heated overhead stream to obtain liquid condensate, and using a sufficient portion of the condensate to reflux the top of the cryogenic distillation column; feeding the first portion of the mixture effluent from the indirect heat exchange into the column at level below the reflux inlet; and feeding a second portion of the mixture directly or indirectly into to the column at level below the inlet of the first portion.

Suitable feed mixtures of organic compounds include any gaseous stream comprising hydrogen, methane, ethylene, C3 hydrocarbons, and optionally acetylene and/or C4 hydrocarbons. Particularly suitable are mixtures comprising olefins produced by thermal cracking of hydrocarbons.

In one aspect of the present invention, the overhead stream is essentially free of C4 hydrocarbons. In another, the overhead stream is essentially free of C3 hydrocarbons. In yet another, the liquid residue from the bottom of the column is essentially free of ethylene. In some cases, it is beneficial that the overhead stream and the liquid residue each contain C3 hydrocarbons.

In a particularly useful aspect of the present invention, the second portion of the mixture is chilled, and the resulting chilled second portion is fed directly or indirectly into to the column at level below the inlet of the first portion. The first portion of the mixture effluent from the indirect heat exchange advantageously is chilled to a temperature at least 5° F lower than the chilled second portion, and the resulting chilled stream is fed directly or indirectly into to the column at level below the reflux inlet.

Another aspect of the present invention is a process for recovery of one or more useful component from a mixture containing a plurality of volatile organic

compounds, which process comprises: providing a fractionation unit comprising a cryogenic distillation column having an overhead outlet and reflux inlet near the top of the column, two or more feed inlets below the reflux inlet, and an outlet for liquid residue from the bottom of the column; fractionating a gaseous mixture comprising hydrogen, methane, ethylene, acetylene, and C3 hydrocarbons to thereby obtain at least an overhead stream comprising a portion of the more volatile components and a liquid residue comprising at least a portion of the less volatile components of the mixture; heating at least a portion of the overhead stream by indirect heat exchange with a first portion of the mixture, compressing at least a portion of the heated overhead stream to an absolute pressure at least 50 percent higher than that in the top of the column; processing the compressed stream to obtain liquid condensate, and using a sufficient portion of the condensate to reflux the top of the cryogenic distillation column; feeding the first portion of the mixture effluent from the indirect heat exchange into the column at level below the reflux inlet; and feeding a second portion of the mixture directly or indirectly into to the column at level below the inlet of the first portion.

Another aspect of special significance is the separation of acetylenic impurities, if any, from the overhead stream. In these cases, processes of the present invention further comprises treating the compressed overhead stream by a process of selective hydrogenation to obtain a compressed stream essentially free of acetylene, and thereafter processing the compressed stream to obtain the liquid condensate.

In yet other aspects of the present invention the gaseous mixture is an effluent stream from a steam cracking unit. In most cases liquid residue from the bottom of the column advantageously is essentially free of ethylene.

The second portion of the mixture beneficially can be chilled, and the resulting chilled second portion is fed directly or indirectly into to the column at level below the inlet of the first portion. In yet another aspect of the present invention, the mixture effluent from the indirect heat exchange is chilled to a temperature at least 5° F lower than the chilled second portion, and the resulting chilled stream is fed directly or indirectly into to the column at level below the reflux inlet.

For a more complete understanding of the present invention, reference should now be made to the embodiments illustrated in greater detail in the accompanying drawing and described below by way of examples of the invention.

## BRIEF DESCRIPTION OF THE FIGURES

The appended claims set forth those novel features which characterize the present invention. The present invention itself, as well as advantages thereof, may best be understood, however, by reference to the following brief description of preferred embodiments taken in conjunction with the annexed drawings, in which:

FIGURE 1 is a schematic diagram of a comparative process for initial fractionation of cracked gas stream containing olefins.

FIGURE 2 is a schematic diagram of an embodiment of this invention in which a cryogenic distillation column in a fractionation unit is used to remove C4 and heavier hydrocarbons from a cracked gas.

It should be noted that only essential separation and heating/cooling steps are shown in these schematic diagrams. Those skilled in the art will recognize that one or more side condensers or side reboilers could be used on any of the embodiments that are described below. These practices are well understood by those skilled in the art and do not constitute an essential part of this invention.

## BRIEF DESCRIPTION OF THE INVENTION

The commercial manufacture of ethylene has taken place for decades, and processes for the production of purified ethylene products have been the subject of much academic and commercial interest. In particular the separation of ethylene from other byproducts produced in its manufacture has been exhaustively studied. There are many commercial methods for recovering and purifying ethylene from a mixed hydrocarbon stream.

The vast majority of ethylene is produced commercially through the steam cracking of hydrocarbons. In a steam cracking furnace a relatively low-pressure hydrocarbon feed is mixed with steam and this mixture is subjected to high temperatures. The hydrocarbons are converted into a furnace effluent gas mixture, also known as cracked gas, which typically comprises ethylene, methane, hydrogen, acetylene and unconverted feed, as well as some hydrocarbons heavier than the feed. The hot furnace effluent gas is cooled by raising high pressure steam and also typically by direct contact with circulated cooled quench oil and/or circulated cooled water. These cooling steps typically condense and at least partially remove relatively heavy hydrocarbons, typically in the naphtha range and heavier.



The uncondensed cooled effluent gas is then directed to a compressor section in which the gas is compressed in one or more stages (typically 3-5 stages) to an elevated pressure. The effluent from each stage is typically cooled against an ambient temperature medium and any condensed liquids removed before entering the subsequent compression stage. Acid gases such as H<sub>2</sub>S and CO<sub>2</sub> are generally removed after one of these stages of compression, for example through the use of a caustic contacting tower or an amine scrubbing system. Once compressed, scrubbed and dried, the furnace effluent gas enters the separation section.

The process of this invention provides for a more energy-efficient method for performing the initial rectification operation for removing relatively heavy hydrocarbons from a mixed gas, for example mixtures containing ethylene and components heavier than ethane. The feed to the initial rectification column is split into at least two streams. At least one of the feed streams is cooled by heat exchange with the rectification column overhead stream. The two or more streams are then separately fed to the initial cryogenic distillation column.

The equipment used for fractionation of the mixture of volatile organics generally includes a cryogenic distillation column that contains mechanical means for enhancing the contacting of the vapor and liquid within the column. These means can include structured or unstructured packing and contacting trays such as bubble-cap, sieve, or valve-type trays. By far the most common type of distillation column is a packed or trayed column in which the liquid and gas streams flow counter-currently in at least a portion of the column. In a typical design, a liquid reflux is introduced at the top of the distillation column and the gas mixture is introduced into a middle section of the column. The liquid residue (containing heavier, less volatile components) exits at the bottom of the column, and the overhead vapor exits at the top of the tower.

In "front-end deethanizer" methods of the invention, the cracked gas is chilled and then directed to a deethanizer distillation column. Within this column components heavier than ethane are removed in the bottoms stream, and the ethane and lighter components, including the desired ethylene product, are recovered in the overhead. The overhead stream can be further compressed if desired, and then is typically further processed in a demethanizer tower and a C<sub>2</sub> splitter tower to recover a purified ethylene product. Acetylene impurities can be removed either before or after processing the stream in a demethanizer column. Front-end deethanizer flowsheets are often utilized when the ethylene is produced from relatively light feedstocks, such as ethane, propane or butane.

“Front-end depropanizer” flowsheets are similar in concept to front-end deethanizer flowsheets, except that the initial rectification column is operated so that essentially all of the C4 and heavier hydrocarbons are recovered in the column bottoms stream. In a “partial depropanizer” column some C3 hydrocarbons can also be recovered in the column bottoms stream. The depropanizer overheads stream therefore contains C3 and lighter components, including ethylene. This stream can be further compressed if desired and is typically further processed within a deethanizer tower, a demethanizer tower, and a C2 splitter tower to recover a purified ethylene product. The order of these subsequent separation steps can vary, but typically the C2 splitter column is the final separation step within the ethylene purification train. Acetylene impurities can be removed either before the subsequent purification steps, or they may be removed from the C2 splitter feed before final purification of the ethylene product. The optimal separation method will depend on many factors, including feed type, product requirements, energy cost, and feed cost, among others.

Because essentially the entire cracked gas stream passes through the front-end rectification operation, it is beneficial to carry out this operation with the highest possible efficiency. We have found a simple yet effective design which significantly improves the energy efficiency of front-end deethanizer and front-end depropanizer columns. This design consists of splitting the front-end rectification column feed into at least two streams. At least one of the streams is chilled through indirect heat exchange with the column overhead. The two or more streams are directed to different points on the front-end rectification column. This design is particularly useful when the overhead stream from the front-end rectification column is to be compressed and/or heated before processing it further.

A benefit of this invention is that it requires less energy than prior-art processes to effect the same desired separation, in particular the removal of C3+ or C4+ hydrocarbons from a cracked gas stream containing ethylene. A further benefit of this invention is that it warms the column overhead stream, thereby allowing a downstream compressor to be constructed of a lower-grade metallurgy than in prior-art processes.

The present invention consists of a new method for cooling and introducing the cracked gas feed to a front-end rectification column while heat-integrating at least one of the feed streams with the column overhead stream. There has now been found a surprisingly large improvement in energy efficiency when combining

a split-feed arrangement with feed/overhead heat integration for a rectification column which recovers the ethylene to the column overhead.

5 This invention is applicable to common front-end deethanizer and front-end depropanizer designs for the initial rectification of cracked gases produced during ethylene manufacture. It is particularly applicable in designs where the overhead of the front-end rectification tower is compressed or heated before being further processed.

10 This invention represents an improved method for removing relatively heavy hydrocarbons from the cracked gas produced in an ethylene manufacturing process. This invention relates to the initial ("front-end") rectification operation to which is directed the dried chilled cracked gas from an ethylene cracking furnace. In particular this invention relates to front-end deethanizer and front-end depropanizer operations. This invention does not relate to front-end demethanizer operations.

15 It is to be noted that while the comparative process and the process of this invention are described in terms of a front-end partial depropanizer operation, those skilled in the art will recognize that the concepts of this invention can be applied to the operation of front-end full depropanizer and front-end deethanizer columns. In these cases the composition of the overhead and bottoms streams will be different from those described herein under, and certain optimal operating conditions may be different. However, the basic concepts of split-feed operation and heat integration of the feed stream with the column overhead are generally applicable to front-end deethanizer front-end full depropanizer, and front-end partial depropanizer columns.

25 Processes of this invention are suitable for use in recovery and separation of organic compounds from a mixture comprising volatile organic compounds. Processes of this invention are particularly suitable for use in fractionation of dried, chilled gaseous mixtures from the thermal cracking of hydrocarbons, for example, cracked gas from a steam cracking furnace.

### 30 BRIEF DESCRIPTION OF PREFERRED EMBODIMENTS OF THE INVENTION

While this invention is susceptible of embodiment in many different forms, this specification and accompanying drawings disclose only some specific forms as an example of the use of the invention. In particular, a preferred embodiment of the invention for recovery and partial separation of components from a mixture

35

of volatile organic compounds is illustrated and described. The invention is not intended to be limited to the embodiment so described, and the scope of the invention will be pointed out in the appended claims.

5 The apparatus of this invention is used with certain conventional components the details of which, although not fully illustrated or described, will be apparent to those having skill in the art and an understanding of the necessary function of such components. Various values of compositions, flow rates, temperatures, and pressures are given in association with a specific example described below; those conditions are approximate and merely illustrative, and are  
10 not meant to limit the invention.

For purposes of comparison only, an exemplary process is described below with reference to FIGURE 1 and compared with the inventive process depicted in FIGURE 2. More specifically with reference to FIGURE 1, which  
15 illustrates a cryogenic distillation column of a fractionation unit in which a single-feed, front-end, partial depropanizer is utilized to remove C3 and heavier hydrocarbons from a cracked gas.

A gaseous mixture comprising hydrogen, methane, ethylene, ethane, acetylene, C3 hydrocarbons, and C4+ hydrocarbons, from a source of cracked gas (not shown), enters exchanger 2 in stream 1. The mixture is chilled in  
20 exchanger 2, and a chilled effluent therefrom in stream 3 is fed into the partial depropanizer column 4. In practice exchanger 2 could represent a series of exchangers in which the cracked gas is chilled in stages through heat exchange with cold process streams and/or various levels of external refrigeration. Liquid residue is withdrawn from the column in bottoms stream 5. The liquid residue  
25 comprises C4+ hydrocarbons and a portion of the C3 hydrocarbons that enter in stream 3. Stream 5 is essentially free of C2 and more volatile, lighter, components. It can be processed further to recover desired products such as propylene, butenes, butadiene, and naphtha if desired. Stripping vapor is provided to column 4 with reboiler 6.

30 Overhead stream 7 from the top of the column comprises hydrogen, methane, ethylene, ethane, acetylene, and C3 components. Stream 7 is essentially free of C4 and less volatile, heavier hydrocarbons. Stream 7 is directed to compressor 8 to produce compressed overhead stream 9. Because this compressed stream contains both hydrogen and acetylene, it can be directed into  
35 an acetylene hydrogenation unit 10. The detailed design and operation of an acetylene hydrogenation unit is well-known to those skilled in the art and is not

described in detail herein. An acetylene hydrogenation unit will generally involve heating or cooling of stream **9** to achieve a desired temperature, selective hydrogenation of the acetylene over a Pd-based catalyst in one or more reactors, and the subsequent cooling of the essentially acetylene-free reactor effluent.

5           The essentially acetylene-free reactor effluent in stream **11** is chilled and partially condensed in exchanger **12**. In practice exchanger **12** could represent a series of exchangers in which the acetylene-free reactor effluent is chilled in stages through heat exchange with cold process streams and/or various levels of external refrigeration such as a propylene refrigeration system. The chilled and  
10 partially condensed stream **13** is directed to separation drum **14** in which vapor and liquid are separated. The vapor exits in stream **15** and is processed further to recover ethylene and other desired products. The condensed liquid in stream **16** is apportioned into two streams. Stream **17** is directed as reflux into the top of column **4**. The pressure of stream **17** is reduced through valve **18** to a suitable  
15 level before entering column **4** as stream **17a**. If there is more liquid in stream **13** than is required as reflux to column **4**, a portion of the condensed overhead liquid is withdrawn in stream **19**. This stream would be further processed to recovery ethylene and other desired products.

FIGURE 2 depicts an embodiment this invention in which a split-feed, front-  
20 end, partial depropanizer is utilized to remove C3 and heavier hydrocarbons from a cracked gas. The overhead stream is essentially free of C4+ hydrocarbons, and the liquid residue from the column bottom is essentially free of C2 and lighter compounds. C3 components are present in both the column overhead stream and bottom residue stream. The overhead stream from the top of the column is  
25 compressed before being processed and condensed to provide reflux liquid to the top of the column.

A gaseous mixture comprising hydrogen, methane, ethylene, ethane, acetylene, C3 hydrocarbons, and C4+ hydrocarbons, from a source of cracked gas (not shown) in stream **100** is divided into streams **101** and **102**. Stream **101** is  
30 chilled in exchanger **103** to produce stream **104** which enters at a lower location on the partial depropanizer column **105**. Stream **102** is directed to exchanger **106** where it is chilled by indirect heat exchange with the column overhead stream. The chilled stream **107** is typically at a lower temperature than stream **104**. Stream **107** is directed to an upper location on the partial depropanizer column  
35 **105**.

A liquid residue stream **108** is withdrawn from the bottom of column **105**, and comprises C4+ hydrocarbons and optionally a portion of the C3 hydrocarbons in stream **100**. Stream **108** is essentially free of C2 or lighter components. It can be processed further to recover desired products such as propylene, butenes, butadiene, and naphtha if desired. Stripping vapor is provided to column **105** with reboiler **109**.

Overhead stream **110** comprising hydrogen, methane, ethylene, ethane, acetylene, and C3 components is essentially free of C4 and heavier hydrocarbons. It is directed into exchanger **106** where it is warmed by heat exchange with feed stream **102**. The warmed overhead stream **111** is directed to compressor **112** to produce compressed stream **113** which is directed to the acetylene hydrogenation unit **114**. The selective acetylene hydrogenation process of unit **114** will generally involve heating or cooling of stream **113** to achieve a suitable temperature for selective hydrogenation of the acetylene over a Pd-based catalyst in one or more reactors, and the subsequent cooling of the essentially acetylene-free reactor effluent.

The essentially acetylene-free reactor effluent stream **115** is chilled and partially condensed in exchanger **116**. In practice exchanger **116** could represent a series of exchangers in which the acetylene-free reactor effluent is chilled in stages through heat exchange with cold process streams and/or various levels of external refrigeration. The chilled and partially condensed stream **117** is directed into separation drum **118** wherein vapor is separated from the liquid condensate. The vapor exits as stream **119** and is processed further to recover ethylene and other desired products. The liquid condensate in stream **120** is divided into two streams. Stream **121** is directed as reflux to the top of column **105**. The pressure of stream **121** is reduced through valve **122** before entering column **105** as stream **121a**. If there is more liquid condensate in stream **117** than is required as reflux to column **105**, a portion of the liquid condensate can be withdrawn as stream **123**. This stream would be further processed to recovery ethylene and other desired products.

It will be further recognized by those skilled in the art that once the general concept of the front-end partial depropanizer column operation depicted for the embodiment of this invention in FIGURE 2 is grasped, it can also be implemented on the other embodiments of this invention, for example front-end full depropanizer, and front-end deethanizer configurations as well.

## EXAMPLE OF THE INVENTION

The following Example will serve to illustrate a certain specific embodiment of the herein disclosed invention. This Example should not, however, be construed as limiting the scope of the novel invention as there are many variations which may be made thereon without departing from the spirit of the disclosed invention, as those of skill in the art will recognize.

## General

To demonstrate several beneficial aspects of the present invention, both the comparative process depicted in FIGURE 1 and the embodiment of FIGURE 2 were simulated using commercially available process simulation software. The mixed hydrocarbon gas feed was derived from the effluent from a battery of steam cracking furnaces cracking a mixture of ethane, propane, and naphtha. The furnace effluent was quenched, cooled, dried, purified of acid gases, and chilled to 25°F against propylene refrigerant and cold process streams before entering the simulations.

In both simulations the partial depropanizer column had 31 theoretical stages, the single-stage compressor outlet pressure was 530 psig, and the liquid product from the partial depropanizer (stream 18 of FIGURE 1 and stream 123 of FIGURE 2) was about 20,000 lb/hr.

Feed stream 1 was chilled to approximately negative 1°F before entering the partial depropanizer column at theoretical stage 15 (as numbered with stage 1 at the top of the column and stage 31 at the bottom of the column). Stream compositions of the process are given in Table 1. Table 2 presents a summary of the compressor and heat exchanger duties for the process of FIGURE 1. Stream and unit numbers in Tables 1 and 2 correspond to those of FIGURE 1.

For the process of this invention as embodied in FIGURE 2, the feed was divided such that the upper feed stream 102 comprises 60 percent of stream 100. The 60 percent portion was cooled to negative 35°F before entering the partial depropanizer at theoretical stage 10. The 40 percent portion in lower feed 101 is cooled to 0°F before entering the partial depropanizer at theoretical stage 16. The stream compositions of the process of this invention are given in Table 3. Table 4 presents a summary of the compressor and heat exchanger duties for process of this invention. Stream and unit numbers in Tables 3 and 4 correspond to those of FIGURE 2.

Note that heat exchanger **12** and exchanger **116** are shown as single heat exchangers in FIGURE 1 and FIGURE 2, respectively, but were modeled as a series of heat exchangers cooled by various levels of propylene refrigerant. The duties presented for these exchangers in Tables 2 and 4 correspond to the sum of  
5 these various individual exchangers.

The total compressor horsepower, as calculated for each process, included the power required by the respective compressors shown in the Figures, and also for the propylene refrigerant compressor which is used to deliver the required chilling duties for exchangers **2** and **12** in FIGURE 1, and exchangers **103**, and  
10 **116** in FIGURE 2. The total compressor horsepower requirement for the comparative process was 22,382 HP. The total compressor horsepower requirement for the process of this invention was 21,291 HP. This result was an energy savings of over 1,000 HP for this invention.

The energy savings provided by the process of this invention was clearly  
15 unexpected and counter-intuitive, because the energy requirement of the compressor **112** of the present invention is actually 1,308 HP higher than the energy requirement of compressor **8** of the comparative process. Even though this process compressor energy requirement was higher for the process of this invention, it is more than offset by a reduction in energy requirement for the  
20 propylene refrigeration compressor brought about by the more efficient heat integration of this invention. This more efficient heat integration allows for a much smaller reflux stream in the process of this invention (compare stream **121** of Table 3 with stream **17** of Table 1).

It is also clear from the data in Tables 1 and 3 that the feed to the  
25 compressor **112** of the process of this invention (see stream **111** in Table 3) was warmer than the feed to compressor **8** (see stream **7** in Table 1). Advantageously, compressor **112** of the present invention could be made of a lower-grade metallurgy than that of compressor **8**.

An Example has been presented and hypotheses advanced herein in order  
30 to better communicate certain facets of the invention. The scope of the invention is determined solely by the scope of the appended claims.

For the purposes of the present invention, "predominantly" is defined as more than about fifty percent. "Substantially" is defined as occurring with sufficient frequency or being present in such proportions as to measurably affect macroscopic  
35 properties of an associated compound or system. Where the frequency or



proportion for such impact is not clear, substantially is to be regarded as about twenty per cent or more. The term "a feedstock consisting essentially of" is defined as at least 95 percent of the feedstock by volume. The term "essentially free of" is defined as absolutely except that small variations which have no more than a negligible effect on macroscopic qualities and final outcome are permitted, typically up to about one percent.

Table 1

Stream No.	1	3	5	7	13	15	16	17	19
Temperature (Deg F)	25.0	-0.8	191.4	-38.8	-14.4	-14.4	-14.4	-14.4	-14.4
Pressure (psig)	210	204	203	200	514	514	514	514	514
Vapor Fraction	0.99	0.97	0.00	1.00	0.86	1.00	0.00	0.00	0.00
<b>Molar flows (lb mol/hr)</b>									
CO	32.6	32.6	0.0	33.3	33.3	32.5	0.8	0.7	0.1
HYDROGEN	8596.9	8596.9	0.0	8671.7	8319.8	8231.2	88.5	74.8	13.8
METHANE	4714.5	4714.5	0.0	4940.4	4940.4	4672.9	267.5	225.9	41.6
ETHYLENE	9355.3	9355.3	0.0	11206.4	11420.4	9228.5	2191.9	1851.2	340.7
ETHANE	2505.8	2505.8	0.2	3216.6	3277.2	2435.4	841.8	711.0	130.8
ACETYLENE	274.6	274.6	0.0	274.6	0.0	0.0	0.0	0.0	0.0
PROPYLENE	882.2	882.2	161.5	1296.5	1313.2	631.4	681.8	575.8	106.0
PROPANE	206.1	206.1	45.3	307.7	307.7	133.7	174.0	147.0	27.0
PROADIENE	16.5	16.5	4.9	19.6	15.8	6.3	9.5	8.0	1.5
METHYLACETYLENE	30.6	30.6	14.1	21.4	8.6	2.8	5.7	4.8	0.9
ISOBUTANE	1.9	1.9	1.9	0.0	0.0	0.0	0.0	0.0	0.0
ISOBUTENE	41.9	41.9	41.9	0.1	0.1	0.0	0.1	0.0	0.0
1,3 BUTADIENE	321.3	321.3	321.2	0.1	0.0	0.0	0.0	0.0	0.0
BUTENE -1	42.1	42.1	42.2	0.1	0.2	0.0	0.1	0.1	0.0
N BUTANE	4.8	4.8	4.8	0.0	0.0	0.0	0.0	0.0	0.0
T-BUTENE 2	14.2	14.2	14.2	0.0	0.0	0.0	0.0	0.0	0.0
C-BUTENE 2	9.4	9.4	9.4	0.0	0.0	0.0	0.0	0.0	0.0
C5+	319.1	319.1	319.1	0.0	0.0	0.0	0.0	0.0	0.0
Total	27369.8	27369.8	980.5	29988.5	29636.6	25374.9	4261.6	3599.3	662.4

Table 2

Unit	Net Duty
2	-9.90 MMBTU/hr
6	8.88 MMBTU/hr
8	11759 HP
12	-53.86 MMBTU/hr

Table 3

Stream No.	100	102	104	107	108	110	111	117	119	120	121	123
Temperature (Deg F)	25.0	25.0	0.0	-35.0	175.4	-46.4	16.2	-17.1	-17.1	-17.1	-17.1	-17.1
Pressure (psig)	208	208	206	208	203	200	200	516	516	516	516	516
Vapor Fraction	0.99	0.99	0.97	0.92	0.00	1.00	1.00	0.90	1.00	0.00	0.00	0.00
<b>Molar flows (lb mol/hr)</b>												
CO	32.6	19.6	13.1	19.6	0.0	33.0	33.0	33.0	32.5	0.5	0.4	0.1
HYDROGEN	8596.9	5158.2	3438.8	5158.2	0.0	8642.6	8642.6	8304.2	8244.4	59.8	45.6	14.2
METHANE	4714.5	2828.7	1885.8	2828.7	0.0	4854.1	4854.1	4854.1	4671.0	183.1	139.6	43.5
ETHYLENE	9355.3	5613.2	3742.1	5613.2	0.0	10503.0	10503.0	10720.8	9215.6	1505.2	1147.8	357.4
ETHANE	2505.8	1503.5	1002.3	1503.5	0.3	2946.3	2946.3	3003.1	2425.1	578.0	440.8	137.2
ACETYLENE	274.6	164.7	109.8	164.7	0.0	274.6	274.6	0.0	0.0	0.0	0.0	0.0
PROPYLENE	882.2	529.3	352.9	529.3	256.1	932.9	932.9	939.8	537.5	402.3	306.8	95.5
PROPANE	206.1	123.6	82.4	123.6	77.0	202.3	202.3	202.3	106.2	96.1	73.3	22.8
PROPDENE	16.5	9.9	6.6	9.9	8.5	11.6	11.6	9.3	4.6	4.8	3.6	1.1
METHYLACETYLENE	30.6	18.4	12.3	18.4	24.3	7.7	7.7	3.1	1.3	1.8	1.4	0.4
ISOBUTANE	1.9	1.1	0.8	1.1	1.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0
ISOBUTENE	41.9	25.1	16.8	25.1	41.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1,3 BUTADIENE	321.3	192.8	128.5	192.8	321.2	0.1	0.1	0.0	0.0	0.0	0.0	0.0
BUTENE -1	42.1	25.3	16.8	25.3	42.1	0.1	0.1	0.2	0.0	0.1	0.1	0.0
N BUTANE	4.8	2.9	1.9	2.9	4.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0
T-BUTENE 2	14.2	8.5	5.7	8.5	14.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C-BUTENE 2	9.4	5.7	3.8	5.7	9.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C5+	319.1	191.4	127.6	191.4	319.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total	27369.8	16421.9	10947.9	16421.9	1120.8	28408.4	28408.4	28070.0	25238.2	2831.8	2159.4	672.4

**Table 4**

Unit	Net Duty
103	-3.90 MMBTU/hr
106	-16.75 MMBTU/hr
109	10.49 MMBTU/hr
112	13067 HP
116	-46.28 MMBTU/hr

**That which is claimed is:**

1. A process for recovery of one or more useful component from a mixture containing a plurality of volatile organic compounds, which process comprises:

5 (1-a) providing a fractionation unit comprising a cryogenic distillation column having an overhead outlet and reflux inlet near the top of the column, two or more feed inlets below the reflux inlet, and an outlet for liquid residue from the bottom of the column;

10 (1-b) fractionating a mixture of organic compounds to thereby obtain at least an overhead stream comprising a portion of the more volatile components and a liquid residue comprising a portion of the less volatile components of the mixture;

15 (1-c) heating at least a portion of the overhead stream by indirect heat exchange with a first portion of the mixture, processing the heated overhead stream to obtain liquid condensate, and using a sufficient portion of the condensate to reflux the top of the cryogenic distillation column;

(1-d) feeding the first portion of the mixture effluent from the indirect heat exchange into the column at level below the reflux inlet; and

20 (1-e) feeding a second portion of the mixture directly or indirectly into to the column at level below the inlet of the first portion.

2. The process according to claim 1 wherein the mixture of organic compounds is a gaseous stream comprising hydrogen, methane, ethylene, acetylene, C3 hydrocarbons, and C4 hydrocarbons.

25 3. The process according to claim 2 wherein the overhead stream is essentially free of C4 hydrocarbons.

4. The process according to claim 2 wherein the overhead stream is essentially free of C3 hydrocarbons.

5. The process according to claim 2 wherein the liquid residue from the bottom of the column is essentially free of ethylene.

30 6. The process according to claim 2 wherein the overhead stream and the liquid residue each contain C3 hydrocarbons.

7. The process according to claim 1 wherein the second portion of the mixture is chilled, and the resulting chilled second portion is fed directly or indirectly into to the column at level below the inlet of the first portion.

5 8. The process according to claim 7 wherein the first portion of the mixture effluent from the indirect heat exchange is chilled to a temperature at least 5° F lower than the chilled second portion, and the resulting chilled stream is fed directly or indirectly into to the column at level below the reflux inlet.

10 9. A process for recovery of one or more useful component from a mixture containing a plurality of volatile organic compounds, which process comprises:

(9-a) providing a fractionation unit comprising a cryogenic distillation column having an overhead outlet and reflux inlet near the top of the column, two or more feed inlets below the reflux inlet, and an outlet for liquid residue from the bottom of the column;

15 (9-b) fractionating a gaseous mixture comprising hydrogen, methane, ethylene, acetylene, and C3 hydrocarbons to thereby obtain at least an overhead stream comprising a portion of the more volatile components and a liquid residue comprising a portion of the less volatile components of the mixture;

20 (9-c) heating at least a portion of the overhead stream by indirect heat exchange with a first portion of the mixture, compressing at least a portion of the heated overhead stream to an absolute pressure at least 50 percent higher than that in the top of the column;

25 (9-d) processing the compressed stream to obtain liquid condensate, and using a sufficient portion of the condensate to reflux the top of the cryogenic distillation column;

(9-e) feeding the first portion of the mixture effluent from the indirect heat exchange into the column at level below the reflux inlet; and

(9-f) feeding a second portion of the mixture directly or indirectly into to the column at level below the inlet of the first portion.

30 10. The process according to claim 9 which further comprises treating the compressed overhead stream by a process of selective hydrogenation to obtain a compressed stream essentially free of acetylene, and thereafter processing the compressed stream to obtain the liquid condensate.

11. The process according to claim 9 wherein the gaseous mixture is an effluent stream from a steam cracking unit.

12. The process according to claim 9 wherein the liquid residue from the bottom of the column is essentially free of ethylene.

5 13. The process according to claim 9 wherein the second portion of the mixture is chilled, and the resulting chilled second portion is fed directly or indirectly into to the column at level below the inlet of the first portion.

10 14. The process according to claim 13 wherein the first portion of the mixture effluent from the indirect heat exchange is chilled to a temperature at least 5° F lower than the chilled second portion, and the resulting chilled stream is fed directly or indirectly into to the column at level below the reflux inlet.

FIGURE 1

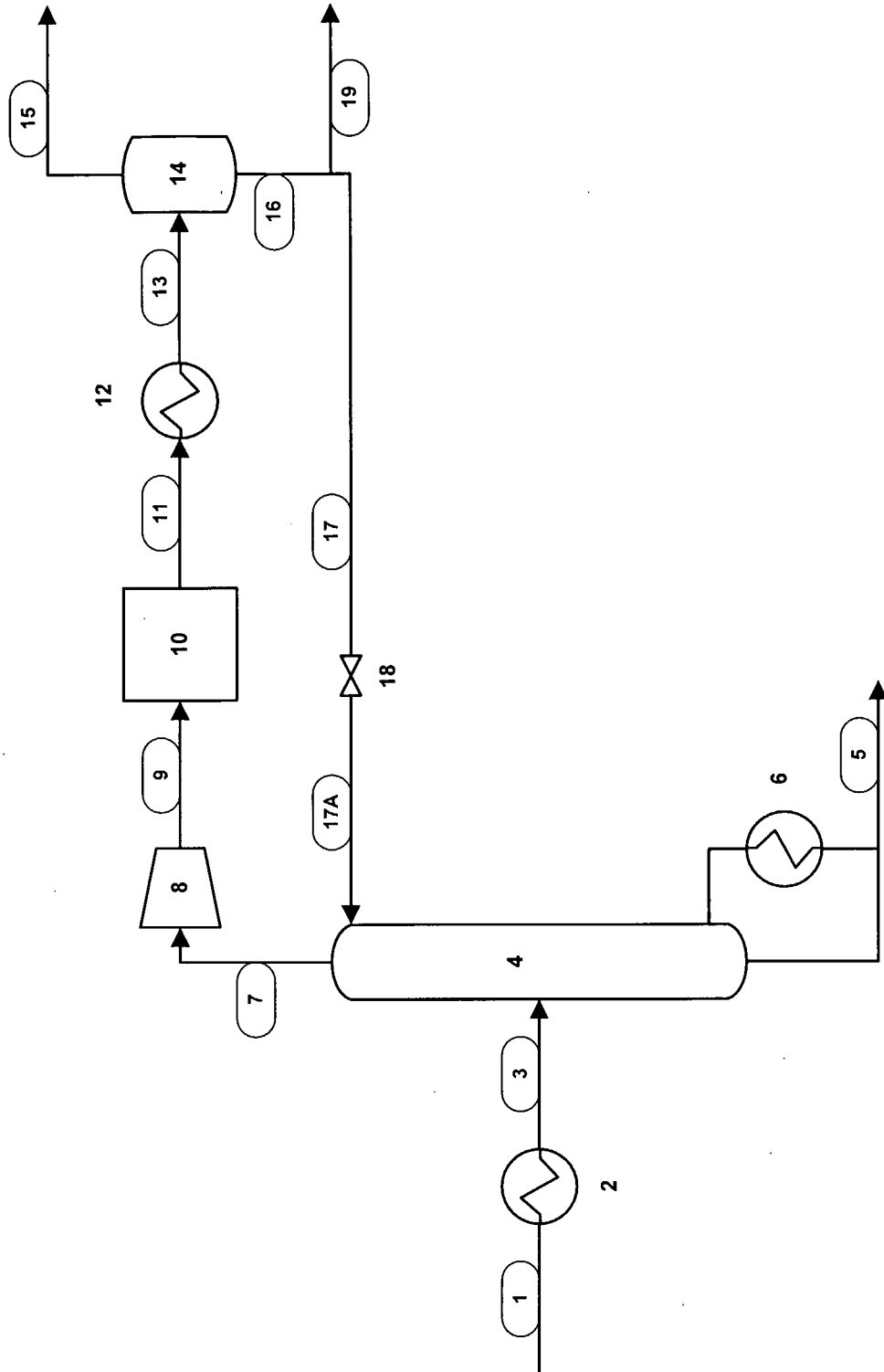
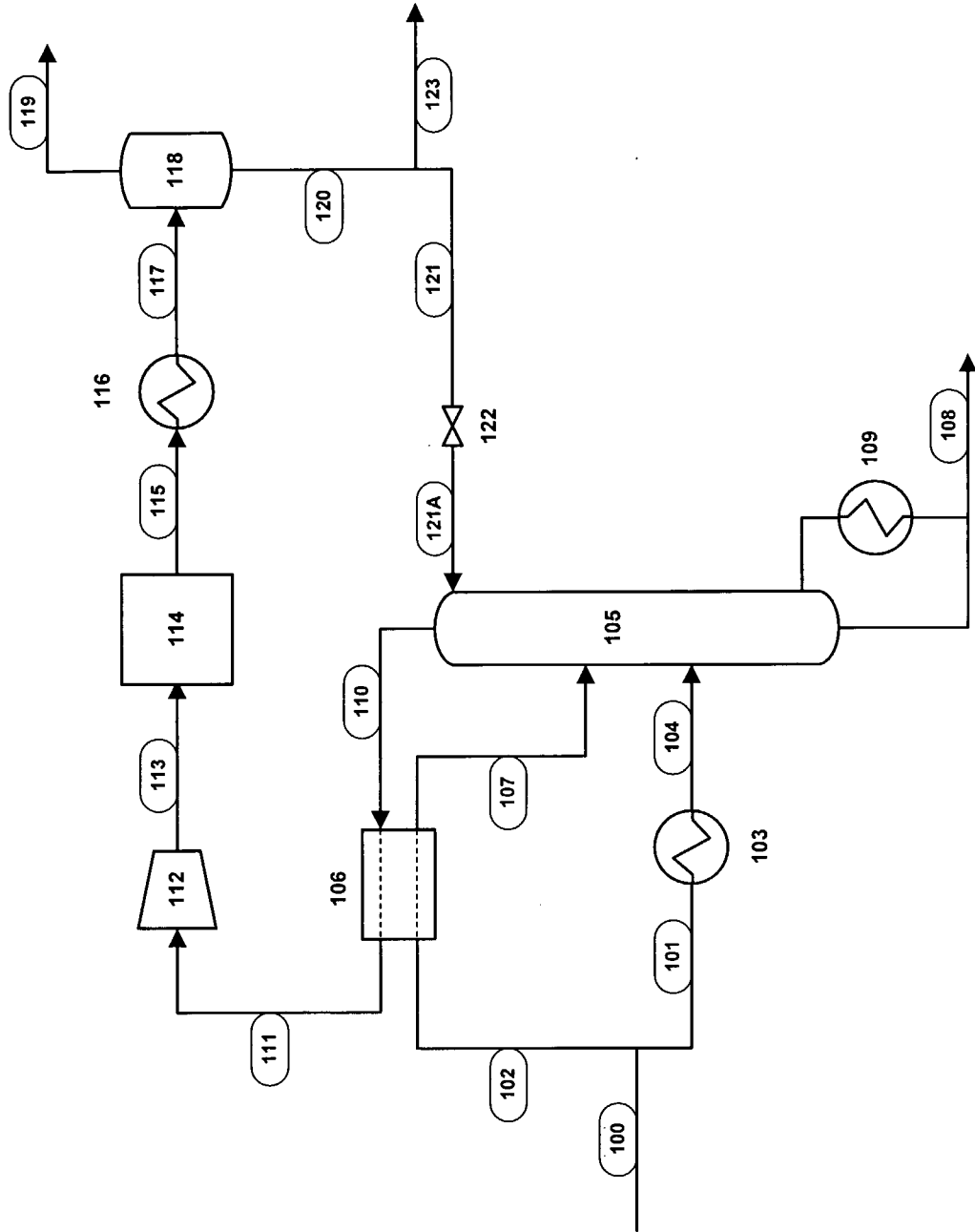




FIGURE 2



# INTERNATIONAL SEARCH REPORT

International application No  
PCT/US2005/026762

**A. CLASSIFICATION OF SUBJECT MATTER**  
 INV. F25J3/02 C07C7/04 C07C11/04 C10G70/04 B01D3/14

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**  
 Minimum documentation searched (classification system followed by classification symbols)  
 F25J C07C C10G B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)  
 EPO-Internal

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	EP 0 288 912 A (AIR PRODUCTS AND CHEMICALS, INC) 2 November 1988 (1988-11-02) figure -----	1-14
A	EP 0 467 860 A (TPL S.P.A) 22 January 1992 (1992-01-22) the whole document -----	1-14
A	US 3 813 890 A (BLIGH B,GB) 4 June 1974 (1974-06-04) figures 4A,4B -----	1-14
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Further documents are listed in the continuation of Box C.       See patent family annex.

\* Special categories of cited documents :

<p>*A* document defining the general state of the art which is not considered to be of particular relevance</p> <p>*E* earlier document but published on or after the international filing date</p> <p>*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>*O* document referring to an oral disclosure, use, exhibition or other means</p> <p>*P* document published prior to the international filing date but later than the priority date claimed</p>	<p>*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>*G* document member of the same patent family</p>
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Date of the actual completion of the international search  <b>29 May 2006</b>	Date of mailing of the international search report  <b>06/06/2006</b>
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer  <b>Göritz, D</b>
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INTERNATIONAL SEARCH REPORT

International application No  
PC1/US2005/026762

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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