

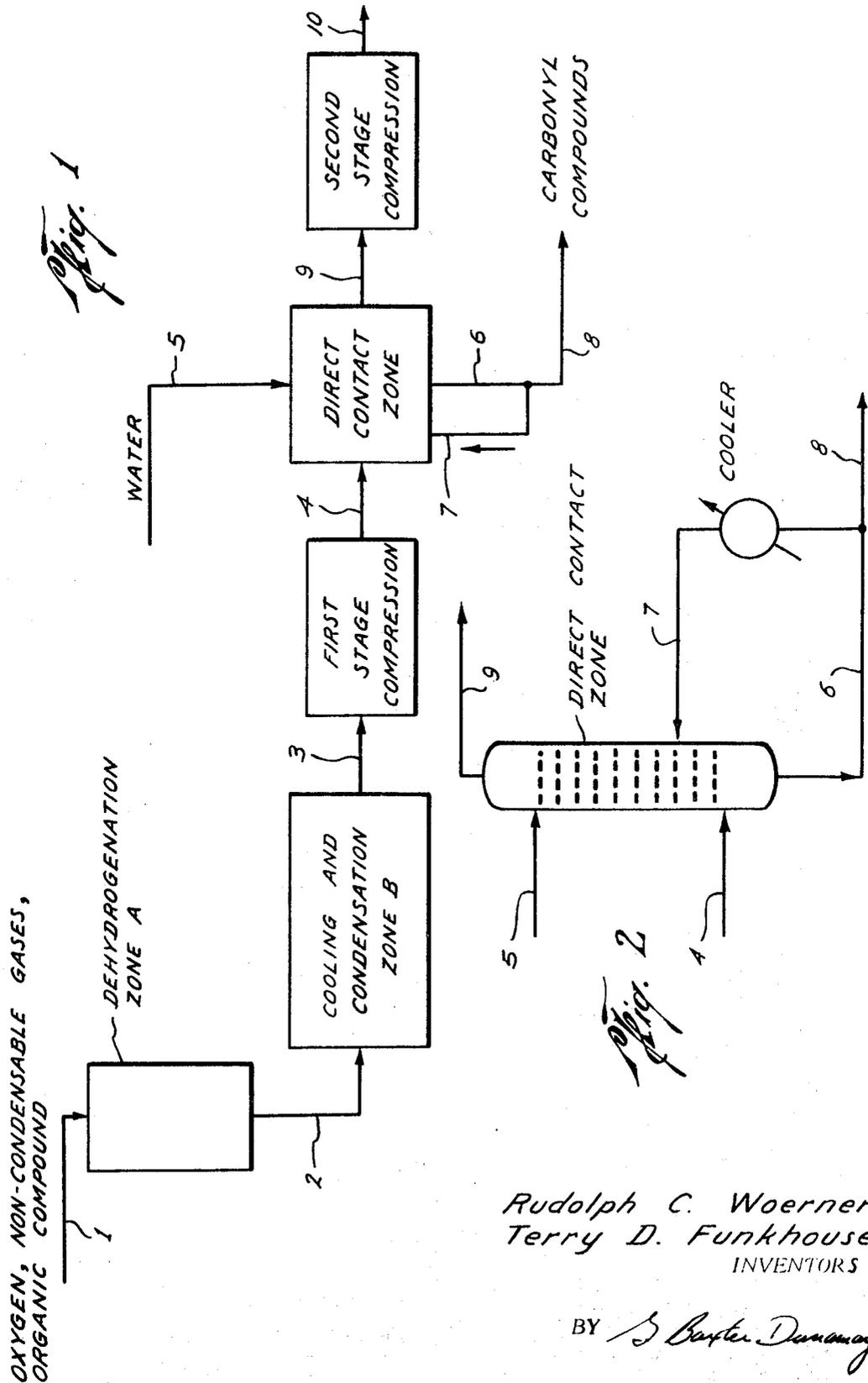
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FOULING REDUCTION IN OXIDATIVE DEHYDROGENATION PROCESS

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FOULING REDUCTION IN OXIDATIVE DEHYDROGENATION PROCESS

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ABSTRACT OF THE DISCLOSURE

Reducing fouling of compressor pistons and cylinders used for the compression of gaseous compositions comprising unsaturated organic compounds and carbonyl compounds by compressing the gaseous composition with a multistage compressor with direct contact scrubbing of gases between compression stages. Preferred source of gaseous composition is from oxidative dehydrogenation process.

BACKGROUND OF THE INVENTION

(1) Field of the invention

This application relates to the mechanical compression of gaseous compositions comprising unsaturated organic compounds and carbonyl compounds. The process is particularly applicable to process for the purification of gases obtained by the oxidative dehydrogenation of organic compounds such as hydrocarbons.

(2) Description of the prior art

It is known to dehydrogenate organic compounds by contacting the organic compound at an elevated temperature with oxygen, such as disclosed in U.S. Pats. Nos. 3,270,080; 3,303,234; 3,303,235; 3,303,236; 3,303,238; 3,308,182 through 3,308,201; 3,324,195; 3,334,152 and 3,342,890.

The dehydrogenation zone effluent from these oxidative dehydrogenation processes may be purified by a process including cooling such as by quench, waste heat boilers and the like and generally the next step is to remove a major portion of the water by condensation. Thereafter the gases are compressed in a compressor. However, in these processes considerable difficulty has been encountered due to fouling of the compressor cylinders, pistons and valves. On a periodic basis it has been necessary to disassemble the compressor and clean the contact surfaces in order to prevent breakage due to fouling and plugging. Further, the operation of the compressor is less efficient during build-up of the fouling because, for example, the valves will not properly open and close. Scoring of the piston and cylinder is also possible. It is known to cool compressed gases between compression stages. For example, the gases between stages may be cooled by indirect heat exchangers in order that the second stage compression step be operated at a lower temperature.

DESCRIPTION OF PREFERRED EMBODIMENTS

The reason for the fouling in the compressor is not fully understood. However, it is believed that the main source of fouling is due to the presence of the various oxygenated compounds and/or unsaturated organic compounds in the gaseous stream being compressed.

A preferred embodiment is illustrated in FIG. 1 of the drawing. A gaseous mixture of the compound to be dehydrogenated, air and steam are fed by line 1 to the dehydrogenation zone A. The dehydrogenation reaction may be conducted in the absence of contact catalysts, but

better results are obtained if the reaction is conducted in the presence of metal or metal compound catalysts, such as disclosed in the patents cited herein. The dehydrogenation reactor may be a fixed or fluid bed reactor. The conditions of reaction may be as disclosed in any of the cited patents such as U.S. 3,334,152. For convenience, the invention will be illustrated for the dehydrogenation of hydrocarbons but it is understood that other dehydrogenatable organic compounds may be substituted in the example.

The effluent 2 from the dehydrogenation zone will contain the impure unsaturated hydrocarbon products, various impurities including oxygenated hydrocarbons, noncondensable gases¹ and perhaps some unconverted hydrocarbon, oxygen and steam. When air is used as the source of oxygen, nitrogen will be present in relatively large quantities as a noncondensable gas. Steam may optionally be present in an amount up to 95 mol percent of the total effluent, such as from about 5 to 96 mole percent. The organic phase including dehydrogenated product, any unreacted feed, oxygenated hydrocarbons, polymer and tar and precursors thereof and any organic decomposition products usually range from about 1 to 50 mole percent of the effluent and generally will be within the range of or about 3 to 30 or 35 mol percent of the effluent. The noncondensable gases, such as nitrogen or CO₂, will usually be present in an amount of from about 20 to 93 mol percent of the total effluent, but more often will be within the range of about 40 to 80 mol percent.

The effluent gases 2 leaving the dehydrogenation zone will generally be at a temperature of about or greater than 600° F. or 700° F. to 1600° F. depending upon the particular dehydrogenation process. The reactor effluent may be cooled by any means or combination of means in cooling and condensation zone B as by quenching, waste heat boilers, condensers, vapor separators, and the like in any sequence. Preferably, the major portion of any water present in the effluent will be removed as condensed steam from the gaseous effluent during this cooling and condensation operation. This cooled gaseous stream 3 may preferably then be compressed. The invention is not restricted to the particular processes prior to compression. For example, an oil quench or other step may be included.

The gaseous composition 3 to be fed to compression will usually comprise, exclusive of any water present, about or from 3.5 to 80 mol percent of unsaturated organic compounds such as hydrocarbon, about or from 0.0005 to 2.5 mol percent of carbonyl compounds,² and optionally about or from 20 to 93 mol percent of noncondensable gases (i.e., noncondensable under the condition at point 3), all based on the total mols of gaseous composition 3 being fed to the compressor, exclusive of any water. Included in the noncondensable gases will be any nitrogen, oxygen, CO or CO₂, and the like. The oxygen content may vary, but suitably will be less than 10 mol percent of stream 3. Steam may also be present in stream 3 in an amount from 0 to 20 or up to such as 50 mol percent or more of the gaseous composition 3. Also present in the gaseous mixture 3 may be unconverted hydrocarbons such as olefins or saturated hydrocarbons and hydrocarbon by-products.

¹The term "noncondensable" or "inert noncondensable" gases refers to those gases, other than hydrocarbons such as nitrogen, CO₂ and CO, which do not condense under the conditions encountered.

²Except where expressed otherwise, all references in the application are to overall quantities of carbonyl compounds as determined by ASTM Method D-1089 and reported as acetaldehyde. Generally, the carbonyl compounds will have from 2 to 8 carbon atoms, e.g., from 2 to 6 carbon atoms when a C₄ to C₆ compound is being dehydrogenated, and will have from 1 to 2 carbonyl groups.

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A preferred composition 3 to be fed to the first stage compressor will comprise, exclusive of any water present, about or from 5 to 65 mol percent of unsaturated hydrocarbons, about or from 0.005 to 1.2 mol percent of carbonyl compounds and about or from 45 to 89 mol percent of the noncondensable gases. A particularly preferred composition 3 contains about or from 8 to 65 mol percent butadiene-1,3, about or from 0.1 to 40 mol percent butene, and about or from 40 to 75 mol percent nitrogen. The composition of the compressed gases at 4 may be within the same ranges as given for point 3.

Compression may be by any suitable multistage mechanical compressors such as reciprocating or centrifugal compressors, with the invention being particularly suitable for reciprocating compressors. The invention is particularly suitable for use with double acting pistons. Although the invention is illustrated in the drawing utilizing a two stage compressor it is understood that more than two stages may be employed if desired. If more than two stages are used preferably a direct contact zone will be between the first and second stages but may be incorporated between any stages and more than one direct contact zone may be employed. Indirect cooling means may also be employed in conjunction with the direct cooling of this invention. Compressors conventionally employed in the recovery of butadiene-1,3 are suitable such as Clark reciprocating compressors. Preferred are compressors which have the cylinders cooled with a water jacket. The pressure and temperature of the gases discharging from each stage of compression will depend upon the particular compressor employed, the pressure and type of equipment downstream from the compressor, the temperature of cooling water available and the like, but typically the compressed gasses from the last stage will be at a temperature of at least 125° F. and a pressure of at least 75 p.s.i.g. but generally the temperature will be at least 175° F. and the pressure at least 100 p.s.i.g.

After at least one stage of compression and before at least one stage of compression the gases are scrubbed in a direct contact zone. Normally, the scrubbing liquid will be water or an aqueous composition but other liquids which will dissolve carbonyl compounds may be used. The contacting zone may be any device for intimately contacting the gases with the scrubbing liquid such as packed towers, open spray towers, tray type columns and other devices for liquid-gas contact known to those skilled in the art.

A portion of the discharge liquid is recycled to the contacting zone. It has been found that recycling of this liquid increases carbonyl removal and reduces the amount of liquid 5 which must be fed to the tower. It has been found also that recycling of the liquid increases carbonyl removal to a greater extent than would increasing the number of actual or theoretical trays in a scrubbing tower particularly when there is a limited quantity of scrubbing liquid 5. Preferably the recycled liquid should be cooled by at least 5° C. but normally will be cooled by at least 10° C. Normally, at least 10 percent by weight and preferably at least 25 percent of the discharge water 6 is recycled to the direct contact zone e.g. as stream 7. In terms of the water not recycled preferably the stream 8 will amount to at least 40 or 50 percent by weight of the stream 6.

The scrubbed gasses 9 are then passed to the next stage of compression and the compressed gases may be further processed as desired.

The process of this invention may be applied to the recovery of products produced by the dehydrogenation of a wide variety of organic compounds. Such compounds normally will contain from 2 to 20 carbon atoms, at least one



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grouping, a boiling point below about 350° C., and such compounds may contain other elements, in addition to carbon and hydrogen such as halogens, nitrogen and sulphur. Preferred are compounds having from 2 to 12 carbon atoms, and especially preferred are compounds of 3 to 6 or 8 carbon atoms.

Among the types of organic compounds which may be dehydrogenated by means of the process of this invention are nitriles, amines, alkyl halides, alkyl aromatic compounds, alkyl heterocyclic compounds, cycloalkanes, alkanes alkenes, and the like. Illustration of dehydrogenations include propionitrile to acrylonitrile, ethyl chloride to vinyl chloride, methyl isobutyrate to methyl methacrylate, 2-chlorobutene-1, or 2,3 dichlorobutane to chloroprene, ethyl pyridine to vinyl pyridine, ethylbenzene to styrene, isopropylbenzene to α -methyl styrene, ethylcyclohexane to styrene, cyclohexane to benzene, methane to ethylene and acetylene, ethane to ethylene to acetylene, propane to propylene or methyl acetylene, allene, or benzene, isobutane to isobutylene, n-butane to butene and butadiene-1,3, butene to butadiene-1,3 and vinyl acetylene, methyl butene to isoprene, cyclopentane to cyclopentene and cyclopentadiene-1,3, n-octane to ethyl benzene and ortho-xylene, monomethylheptanes to xylenes, propane to propylene to benzene, 2,4,4-trimethylpentane to xylenes, the formation of new carbon to carbon bonds by the removal of hydrogen atoms such as the formation of a carbocyclic compound from two aliphatic hydrocarbon compounds or the formation of a dicyclic compound from a monocyclic compound having an acyclic group such as the conversion of propene to diallyl. Representative materials which are dehydrogenated by the novel process of this invention include ethyl toluene, alkyl chlorobenzenes, ethyl naphthalene, isobutyronitrile, propyl chloride, isobutyl chloride, ethyl fluoride, ethyl bromide, n-pentyl iodide, ethyl dichloride, 1,3-dichlorobutane, 1,4-dichlorobutane, the chlorofluoroethanes, methyl pentane, and the like.

Suitable dehydrogenation reactions are the following: acyclic compounds having 4 to 5 non-quaternary contiguous carbon atoms to the corresponding olefins, diolefins or acetylenes having the same number of carbon atoms; aliphatic hydrocarbons having 6 to 16 carbon atoms and at least one quaternary carbon atom to aromatic compounds, such as 2,4,4-trimethylpentene-1 to a mixture of xylenes; acyclic compounds having 6 to 16 carbons atoms and no quaternary carbon atoms to aromatic compounds such as n-hexane or the n-hexenes to benzene; cycloparaffins and cycloolefins having 5 to 8 carbon atoms to the corresponding olefin, diolefin or aromatic compound, e.g., cyclohexane to cyclohexene or cyclohexadiene or benzene; aromatic compounds having 8 to 12 carbon atoms including one or two alkyl side chains of 2 to 3 carbon atoms to the corresponding aromatic with unsaturated side chain such as ethyl benzene to styrene.

The preferred compounds to be dehydrogenated are hydrocarbons with a particularly preferred class being acyclic non-quaternary hydrocarbons having 3 or 4 to 5 contiguous carbon atoms or ethyl benzene and the preferred products are n-butene-1 or 2, butadiene-1,3, vinyl acetylene, 2-methyl-1-butene, 3-methyl-1-butene, 3-methyl-2-butene, isoprene, styrene or mixtures thereof. Especially preferred as feed are n-butene-1 or 2 and the methyl butenes and mixtures thereof such as hydrocarbon mixtures containing these compounds in at least 50 mol percent.

The organic compound to be dehydrogenated is contacted with oxygen in order for the oxygen to oxidatively dehydrogenate the compound. The oxygen may be supplied to the organic compound from any suitable source as by feeding oxygen to a dehydrogenation zone for example as disclosed in U.S. 3,207,810 issued Sept. 21, 1965. Oxygen may be fed to the reactor as pure oxygen, as air, as oxygen-enriched air, oxygen mixed with diluents, and so forth. Oxygen may also be supplied by means of a transport or moving oxidant type of process such as dis-

closed in U.S. 3,050,572 issued Aug. 21, 1962 or U.S. 3,118,007 issued Jan. 14, 1964. The term oxidative dehydrogenation process when used herein means a process wherein the predominant mechanism of dehydrogenation is by the reaction of oxygen with hydrogen.

The amount of oxygen employed may vary depending upon the desired result such as conversion, selectivity and the number of hydrogen atoms being removed. Thus, to dehydrogenate butane to butene requires less oxygen than if the reaction proceeds to produce butadiene. Normally oxygen will be supplied (including all sources, e.g. air to the reactor or solid oxidant to the reactor) in the dehydrogenation zone in an amount from about 0.2 to 1.5, preferably 0.3 to 1.2, mols per mol of H₂ being liberated from the organic compound. Ordinarily the mols of oxygen supplied will be in the range of from .2 to 2.0 mols per mol of organic compound to be dehydrogenated and for most dehydrogenations this will be within the range of .25 to 1.5 mols of oxygen per mol of organic compound.

Halogen or other additives may be present in the dehydrogenation step such as disclosed in the above cited patents, e.g., U.S. 3,334,152 issued Aug. 1, 1967. Means for separating halogen may also be incorporated in the dehydrogenation reactor or downstream.

Preferably, the reaction mixture contains a quantity of steam or diluent such as nitrogen with the range generally being between about 1 or 2 and 40 mols per mol of organic compound to be dehydrogenated.

The temperature for the dehydrogenation reaction generally will be at least about 250° C., such as greater than about 300° C. or 375° C., and the maximum temperature in the reactor may be about 700° C. or 800° C. or perhaps higher such as 900° C. under certain circumstances. However, excellent results are obtained within the range of or about 350° C. to 700° C., such as from or about 400° C. to or about 675° C. These temperatures are measured at the maximum temperature in the dehydrogenation zone.

The remaining conditions, catalysts, flow rates and the like for oxidative dehydrogenation are known to those skilled in the art and may be e.g., as disclosed in U.S. 3,334,152 issued Aug. 1, 1967, or any of the remaining patents cited herein.

The invention can best be illustrated by a specific example. All references to parts per million (p.p.m.) refer to parts by weight of the total stream referred to. Reference is made to the drawing for the various pieces of equipment and streams. In FIG. 1 a hydrocarbon stream comprising butene-2 as the major component is dehydrogenated to butadiene-1,3 in reactor A. The feed 1 to the reactor includes air and steam. The effluent 2 from the reactor comprises butadiene-1,3, unreacted butene, carbonyl compounds, steam, noncondensable gaseous components such as nitrogen and various dehydrogenation by-products such as CO₂. The effluent is cooled and most of the water is removed in the steam condensation zone B. The gaseous stream is then compressed. The gaseous composition fed to the first stage compressor comprises by mol percent approximately a total of 67 percent noncondensable gases (mostly nitrogen, but also includes the other residual gases of air, as well as CO and CO₂) and 28 percent hydrocarbons. The hydrocarbon portion is primarily C₄'s with butadiene-1,3 being the major component. The composition also contains 5 percent water and 815 p.p.m. acetaldehyde, 440 p.p.m. acrolein and 2 mol percent furan. The discharge from the first stage compressor is at a temperature of 120° C. and a pressure of 2.62 meters of mercury.

The discharge from the first stage compressor is fed to the direct contact zone which is shown in FIG. 1 and for this example in more detail in FIG. 2. The direct contact zone in this example is a tray type scrubber having 12 plates. The compressor first stage discharge 4 is fed below the trays and passes up the tower. Scrubbing water 5 at a temperature of 40° C. is fed to the top of

the tower at a rate of 63 gallons per minute (g.p.m.). The scrubbing water contains approximately 38 p.p.m. of acetaldehyde and 21 p.p.m. acrolein.

In the tower the gases are scrubbed and cooled. The discharge aqueous composition 6 is at a temperature of 52° C. and a portion of this is recycled to the tower. In this example the composition to be recycled 7 is cooled by indirect heat exchange in the cooler and fed to the tower on the tenth tray from the top at a temperature of 42° C. The recycle 7 is fed at approximately 33 g.p.m. and the remainder 8 amounts to 63 g.p.m. The stream 8 contains minor amounts of carbon dioxide and hydrocarbons as well as 362 p.p.m. acetaldehyde and 196 p.p.m. acrolein.

The scrubbed gases 9, taken off overhead, comprise 198 p.p.m. acetaldehyde, 103 p.p.m. acrolein and 0.02 mole percent furan and are at a temperature of 40° C. and a pressure of 2.52 meters of mercury. The scrubbed gases 9 amount to 448 mols per hour and are fed to the second stage of a reciprocating compressor where the gases are compressed to a pressure of 8.72 meters of mercury at a temperature of 121° C. The compressed gases 10 may be treated to further separate and purify the gases such as by extractive distillation, CAA extraction, fractional distillation and the like.

We claim:

1. In a process for the purification of gaseous compositions comprising unsaturated organic compounds and carbonyl compounds wherein the said gaseous composition is compressed with a compressor the improvement comprising compressing the gaseous composition with a multistage compressor with direct contact scrubbing of compressed gases after at least one stage of compression with a liquid wash in a direct contacting zone with at least a portion of the discharge from the contacting zone being recycled to the contacting zone and at least a portion of the discharge from the contacting zone not being recycled to the contacting zone.

2. The process of claim 1 wherein the said gaseous composition has been obtained by the oxidative dehydrogenation of a hydrocarbon.

3. The process of claim 1 wherein the compressor is a reciprocating type compressor.

4. The process of claim 1 wherein the said unsaturated organic compound is a hydrocarbon.

5. The process of claim 1 wherein the said unsaturated organic compound is butadiene-1,3.

6. The process of claim 1 wherein the said gaseous composition being compressed comprises from 3.5 to 80 mol percent of unsaturated hydrocarbon and from about 20 to 93 mol percent noncondensable gases.

7. The process of claim 1 wherein the said gaseous composition being compressed comprises from about .0005 to 2.5 mol percent carbonyl compounds.

8. The process of claim 2 wherein the said oxidative dehydrogenation process is conducted by reacting an organic compound to be dehydrogenated with oxygen and halogen in a dehydrogenation reactor.

9. The process of claim 1 wherein the said portion of the discharge from the contacting zone is cooled before recycling to the direct contact zone.

10. The process of claim 1 wherein the direct contacting zone is a scrubbing tower with the said discharge from the contacting zone being recycled to the lower half of the scrubbing tower.

11. The process of claim 1 wherein the compressor is a two stage compressor and the direct contact scrubbing is between the first and the second stages of compression.

12. The process of claim 1 wherein the direct contacting zone is a tray type tower scrubber and the gases below the bottom tray of the tower scrubber are sprayed with an aqueous spray.

13. The process for the compression of a mixture obtained by the oxidative dehydrogenation of a member selected from the group consisting of propane, n-butane, n-butene, n-pentane, isopentane, methyl butene and mix-

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tures thereof to provide a gaseous mixture comprising on a water free basis from 3.5 to 80 mol percent unsaturated hydrocarbon, from 20 to 93 mol percent noncondensable gases and from about .0005 to 2.5 mol percent carbonyl compounds, the said gaseous mixture being compressed in a two stage compressor with the gaseous composition being scrubbed between stages in a tower with water and with a portion of the discharge scrubber water from said tower being cooled and recycled to the lower half of the said tower and at least 40 percent by weight of the discharge scrubber water from said tower being not recycled to said tower.

14. The process of claim 13 wherein the compound being dehydrogenated comprises n-butene and the dehydrogenated product is butadiene-1,3.

15. The process of claim 1 wherein at least 40 percent

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by weight of the discharge from said contacting zone is not recycled to said contacting zone.

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