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PROCESS FOR RECOVERING OLEFINS FROM CAT-CRACKED GAS WITHOUT ACCUMULATING UNDESIRABLE OXIDES OF NITROGEN

BACKGROUND OF THE INVENTION

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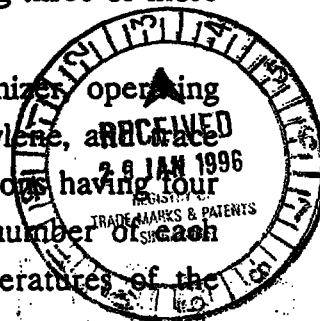
1. Field of the Invention

The present invention relates to the recovery of desired hydrocarbons, preferably olefins, from cat-cracked hydrocarbon gas streams. More particularly, the invention relates to the recovery of olefins from cat-cracked gas streams while avoiding the accumulation of unwanted oxides of nitrogen and their reaction products, such as nitric oxide, nitrogen dioxide, dinitrogen trioxide, nitro gums, ammonium nitrite and ammonium nitrate, Accumulations of these compounds have been observed in ethylene recovery facilities. Such accumulations can cause various operating problems, such as equipment plugging and explosion hazards.

2. Discussion of Background Information

Typically, olefins are recovered from cat-cracked gases using cryogenic fractionation in which the coldest temperatures normally fall well below -107°C (-160°F), and may dip as low as -168°C (-270°F). The feed is fed through a series of units where the components are separated based on boiling point differences. The feed is first fed to a cryogenic demethanizer, operating between -118 to -140°C (-180 to -220°F), where methane with a boiling point of approximately -162°C (-259°F) and hydrogen with a boiling point of approximately -253°C (-423°F) go overhead and hydrocarbons having two or more carbon atoms go bottoms. The demethanizer bottoms is then fed to a deethanizer, operating between -73 to -101°C (-100 to -150°F), where the ethane with a boiling point of approximately -88°C (-127°F), ethylene with a boiling point of approximately -104°C (-155°F) and trace amounts of hydrogen and methane go overhead and hydrocarbons having three or more carbon atoms go bottoms.

The demethanizer bottoms is then fed to a deethanizer, operating between -46 to -73°C (-50 to 100°F), where propane, propylene, and trace amounts of ethane and ethylene go overhead and hydrocarbons having four or more carbon atoms go bottoms. As the hydrocarbon number of each component to be separated increases, the operating temperatures of the



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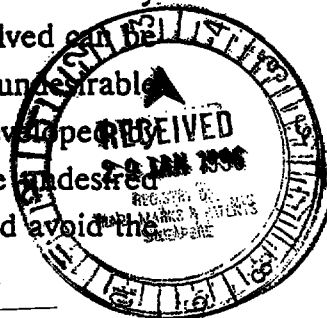


separation towers also increase, because of the higher boiling points of each component.

Unfortunately, cat-cracked gases tend to be contaminated with nitrogen oxides. Nitric oxide (NO) is of concern in cryogenic separation facilities because nitric oxide boils at approximately -152°C (-241°F) which is close to the boiling point temperature of methane at approximately -162°C (-259°F). Thus, nitric oxide tends to follow the lighter compounds contained in the refinery gas stream. At the very low temperatures used during cryogenic fractionation, nitric oxide may be oxidized by oxygen, which typically is present in cat-cracked gases, to form unwanted nitrogen dioxide (NO_2) and dinitrogen trioxide (N_2O_3). If ammonia is present during the cryogenic fractionation process, ammonium nitrite (NH_4NO_2) and ammonium nitrate (NH_4NO_3) may be formed. In the presence of unsaturated hydrocarbons, nitrogen oxides also can react to form NO_x gums.

Nitric oxide and nitrogen dioxide are poisonous gases which are undesirable for obvious reasons. Ammonium nitrite, ammonium nitrate, dinitrogen trioxide, nitrogen dioxide and NO_x gums solidify at the extremely low temperatures used during cryogenic fractionation, and, as a result, may plug the equipment and/or may cause a pressure drop in the system. Ammonium nitrite also has been known to decompose spontaneously at temperatures of around 60°C (140°F), while ammonium nitrate is reported to decompose spontaneously at 210°C (410°F). NO_x gums, particularly those NO_x compounds formed with diolefins, such as butadiene, are reported to be unstable and to explode spontaneously at various temperatures. For all of these reasons, researchers have tried to develop methods to refine cat-cracked gases without accumulating these unwanted nitrogen-based byproducts.

A number of processes have been developed for removing nitrogen based substances from equipment used to refine gases containing oxides of nitrogen. These processes typically are costly and burdensome because they require that the process be shut down so that the equipment involved can be washed or otherwise treated to remove accumulations of the undesirable compounds. Few, if any, preventative processes have been developed which cat-cracked gas may be refined without accumulating the undesired compounds in the first place. A preventative process which would avoid the accumulation of these compounds would be highly desirable.



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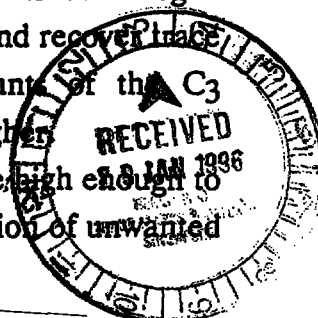
US-A-5,220,097, which was published after the priority date of this application, teaches a process utilizing a demethanizer absorber in a particular configuration to provide a means to reduce the concentration of acetylenes and diolefins which presents a potential for fouling equipment in an olefin recovery process. However, this reference does not teach the presence, accumulation, or removal of nitric oxides. In fact, the only oxides even mentioned are carbon monoxide and carbon dioxide (column 1, lines 15-25).

SUMMARY OF THE INVENTION

The present invention provides a safe, effective, and economical method for recovering olefins from cat-cracked gases without accumulating dangerous amounts of nitrogen oxides. One way to achieve this result is using well known absorber technology to operate the demethanizer rather than using the typical cryogenic technology.

Recovering olefins from cat-cracked gases without the accumulation of dangerous amounts of nitrogen oxides is achievable in a safe, effective, and economical process by conducting the recovery at temperatures that are high enough to prevent the oxidation of nitric oxide (NO) to form nitrogen dioxide (NO₂) and high enough to prevent the accumulation of unwanted nitrogen oxides. A stream of cat-cracked gas first is scrubbed to remove acid gases, including nitrogen dioxide (NO₂), and then is passed through a depropanizer fractionation tower. Hydrocarbons having four or more carbon atoms are recovered in the bottoms of the depropanizer, and the overhead from the depropanizer -- which is composed of hydrocarbons having three or fewer carbon atoms -- is sent to an absorber demethanizer tower. Hydrocarbons having two or more carbon atoms are recovered in the bottoms from the absorber demethanizer tower, where temperatures are no lower than about -45.56°C (-50°F). The overhead from the absorber demethanizer tower -- which is composed of methane, hydrogen, and trace amounts of nitrogen oxide, C₂, and absorbent (C₃) -- then is chilled to condense and recover trace amounts of C₂ and heavier gases, including trace amounts of the C₃ absorbent, at temperatures of about -101.11°C (-150°F) or higher.

Thus the process is conducted at temperatures that are high enough to prevent the oxidation of nitric oxide and avoid the accumulation of unwanted NO_x compounds in the C₂ and heavier hydrocarbon streams.



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BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a simplified flow diagram of a facility in which cat-cracked gases are refined according to the process of the present invention.

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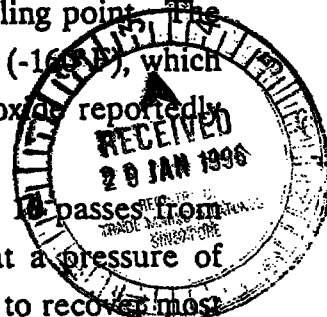
DETAILED DESCRIPTION OF THE INVENTION

With reference to FIG. 1, it should be understood that, when a stream is identified, the stream actually represents a pipeline. Also, it should be understood that the usual flow-control valves, temperature regulatory devices, pumps, heat exchangers, accumulators, condensers, and the like ("auxiliary equipment"), are operating in a conventional manner.

Referring to FIG. 1, after compression and cooling, the cat-cracked gas stream flows through a line 10 to feed a caustic scrubbing tower 11. The stream then is fed to a standard depropanizer tower 12. The gas stream is separated by the depropanizer tower 12 into (1) an overhead containing hydrocarbons having three or fewer carbon atoms (with normal contaminants, such as trace C₄'s) which exits the depropanizer tower 12 via line 16. The processing of the bottoms from the depropanizer tower 12 does not form a part of the present invention, and will not be discussed further. The overhead from the depropanizer tower 12 flows through the line 14 and through various auxiliary equipment and feeds into an absorber demethanizer tower 18.

In a preferred embodiment, the absorbent used in the absorber demethanizer tower 18 is "the C₃ cut". The C₃ cut is a preferred absorbent because the C₃ cut has a high capacity (per pound of absorber oil) to absorb C₂'s at relatively warm temperatures of about -28.89°C (-20°F) to -40°C (-40°F). Also, small quantities of the C₃'s, which are lost in the absorber demethanizer overhead stream, can be recovered by moderate chilling to temperatures of -78.89°C (-110°F) to -90°C (-130°F), or alternately by a second absorption step using an absorbent with a higher boiling point. The temperatures used in the process do not approach -106.67°C (-160°F), which is the temperature at which unwanted compounds of nitric oxide reportedly begin to accumulate.

The overhead from the absorber demethanizer tower 18 passes from the demethanizer tower 18 through a line 20, preferably at a pressure of about 2.8 - 3.4 million Newtons/m² (400 - 500 psi). In order to recover most

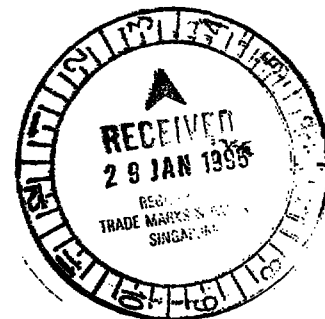




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of the remaining C_2 and C_3 hydrocarbons from the overhead of the absorber demethanizer tower 18, the overhead preferably is cooled using Joule Thomson expansion of the hydrogen/methane gas stream. To accomplish this, the overhead is fed through at least one heat exchanger 22. Then the overhead is depressured to a drum 24 where condensed liquid is separated from the hydrogen/methane gas stream at a temperature of about -78.89°C (-110°F) to -90°C (-130°F) and the liquid containing recovered C_2 's and C_3 's is returned to the demethanizer absorber tower 18 as stream 26 for recovery. The hydrogen/methane overhead from drum 24 is used as the chilling medium in exchanger 22. Because the overhead from the absorber demethanizer tower 18 contains more C_3 hydrocarbons than C_2 hydrocarbons, the condensing temperature of C_2 and heavier portion is not low enough to facilitate the accumulation of undesirable oxides of nitrogen.

One of ordinary skill in the art will recognize that a similar result could be achieved by other means. For example, instead of using Joule Thomson expansion to cool the absorber demethanizer overhead, a second step could be added in which heavier oil was used as an absorbent to recover the C_2 and C_3 hydrocarbons from the overhead. The use of heavier oil as an absorbent also would permit processing at relatively high temperatures and thus would further reduce the risk of unwanted accumulation of nitrogen oxide compounds.



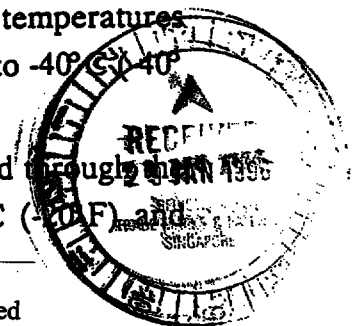


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Claims:

1. A process for reducing the accumulation of undesirable oxides of nitrogen during the recovery of one or more desired hydrocarbons from cat-cracked gas wherein the gas contains oxides of nitrogen comprising the following steps, all conducted at temperatures above -107°C (-160°F):
 - A. removing acid gases from the gas;
 - B. separating the gas into a first portion primarily comprising hydrocarbons having no more than three carbon atoms and a second portion primarily comprising hydrocarbons having at least four carbon atoms;
 - C. separating the first portion using absorption with an absorber oil into a third portion primarily comprising compounds selected from the group consisting of methane, hydrogen, nitric oxide, and a small proportion of hydrocarbons having two and three carbon atoms, and a fourth portion primarily comprising hydrocarbons having at least two carbon atoms; and
 - D. recovering at least one desired hydrocarbon from the third portion.
2. The process of claim 1 wherein the acid gases from step A are removed by passing the gas through an alkaline solution.
3. The process of claim 1 or 2 wherein the gas is separated in step B by passing the gas through a depropanizer to form a first portion and a second portion.
4. The process of claim 1, 2, or 3 wherein the first portion is separated in step C by passing the first portion through an absorber demethanizer to form a third and a fourth portion.
5. The process of any preceding claims wherein the gas is separated in step C into the third portion and the fourth portion at temperatures above -46°C (-50°F), preferably between -29°C (-20°F) to -40°C (-40°F).
6. The process of claim 5 wherein the first portion is passed through an absorber demethanizer at temperatures between -29°C (-20°F) and -40°C (-40°F).

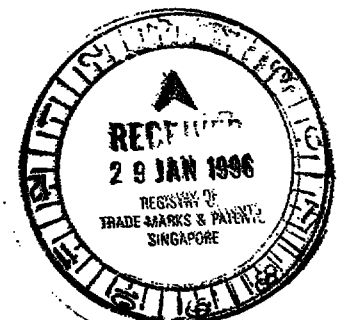
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7. The process of any preceding claims wherein the recovering step D comprises chilling the third portion to a temperature of from -79°C (-110°F) to -101°C (-150°F) whereby the third portion is separated into a fifth portion comprising a fraction enriched in hydrocarbons having two and three carbon atoms and a sixth portion primarily comprising compounds selected from the group consisting of hydrogen, methane, and nitric oxide.
8. The process of claim 7 wherein the chilling step comprises heat exchanging the sixth portion with the third portion after expansion of the third portion.
9. The process of claim 8 wherein said expansion is a Joule Thomson expansion.
10. The process of claim 7, 8, or 9 wherein the temperature of the third portion is reduced to between -79°C (-110°F) and -90°C (-130°F) during the chilling step.
11. The process of any of the preceding claims wherein the desired hydrocarbon is an olefin.
12. The process of any of the preceding claims where the recovering step comprises absorbing said at least one desired hydrocarbon from the third portion using a hydrocarbon absorbent having more than three carbon atoms.
13. The process of any preceding claims wherein the absorber oil used to separate the first portion into the third portion and the fourth portion of step C is a C_3 absorber oil.
14. A process for reducing the accumulation of undesirable oxides of nitrogen during the recovery of one or more desired hydrocarbons from cat-cracked gas wherein the gas contains oxides of nitrogen comprising the use of an absorbent oil in the recovery process whereby the process is conducted at temperatures above -107°C (-160°F).



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