THE AZEO-OCTANE GAS DEHYDRATION PROCESS June 9, 2011

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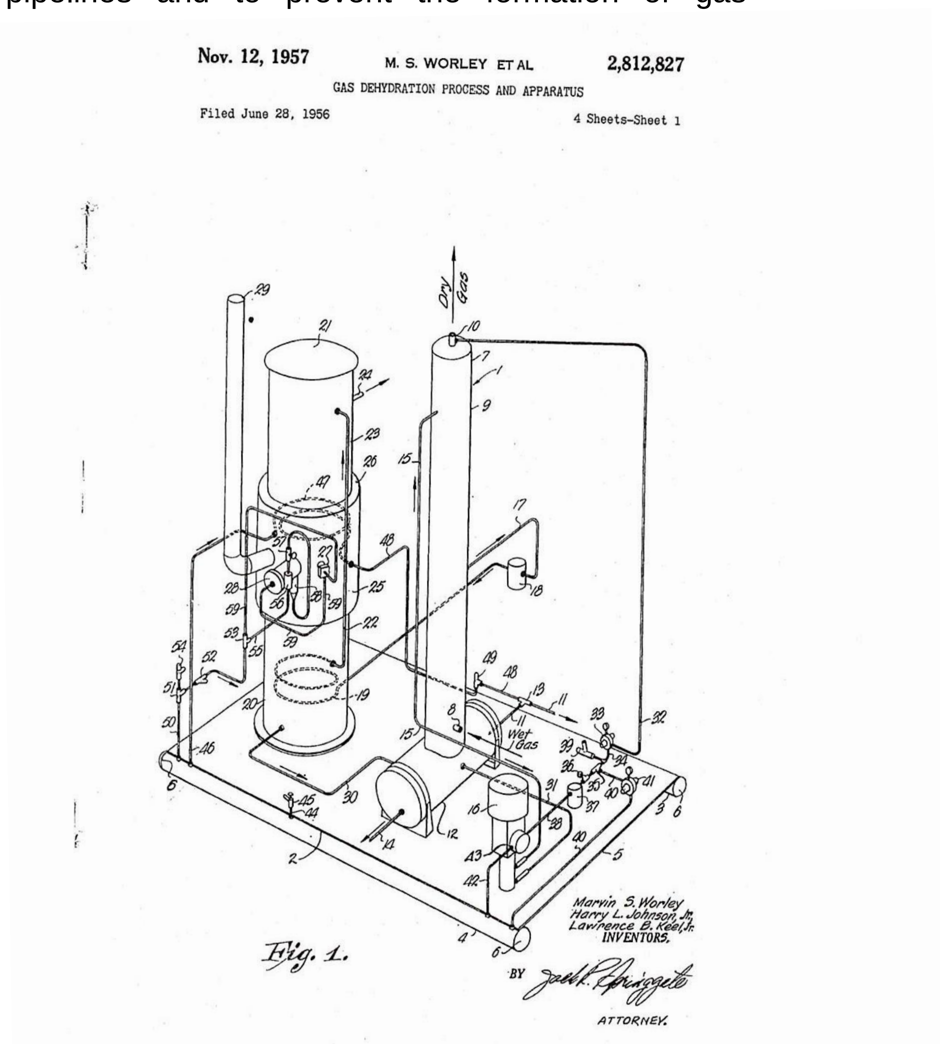
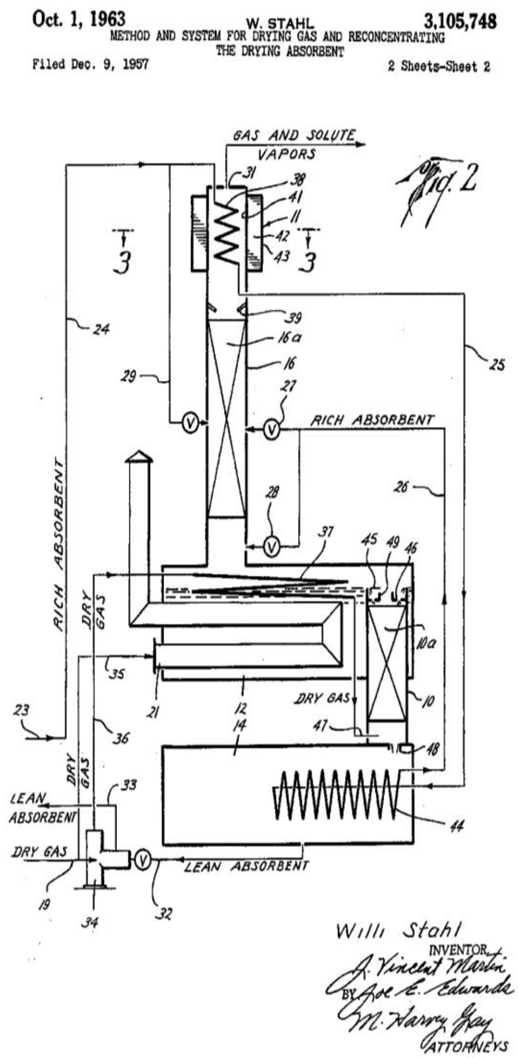
INTRODUCTION

Liquid desiccants such as mono, di and tri-ethylene glycols were first employed in the 1950's to dry natural gases via countercurrent contact in order to reduce corrosion of pipelines and to prevent the formation of gas hydrates that would block pipelines. Regeneration of the liquid desiccant was accomplished by heating the glycol in a reboiler and purifying the glycol in a distillation still column to a glycol purity of up to 98.5%. This allowed the contacted gas to be dryed to a water content of about 10 lbs water per million standard cubic feet of gas. The introduction of sparging natural gas into the reboiler in the late 1950's allowed regeneration systems to attain a glycol purity of 99.4% for a gas water content of about 7 lbs water per MMSCF.



In 1963 Willy Stahl invented the natural gas stripping column (U.S. Patent No.: 3,105,748) for the Parkersburg Rig & Reel Company.

Black, Sivals and Bryson Inc., a competing oil and gas equipment fabricator, liked the idea so much they bought the company.

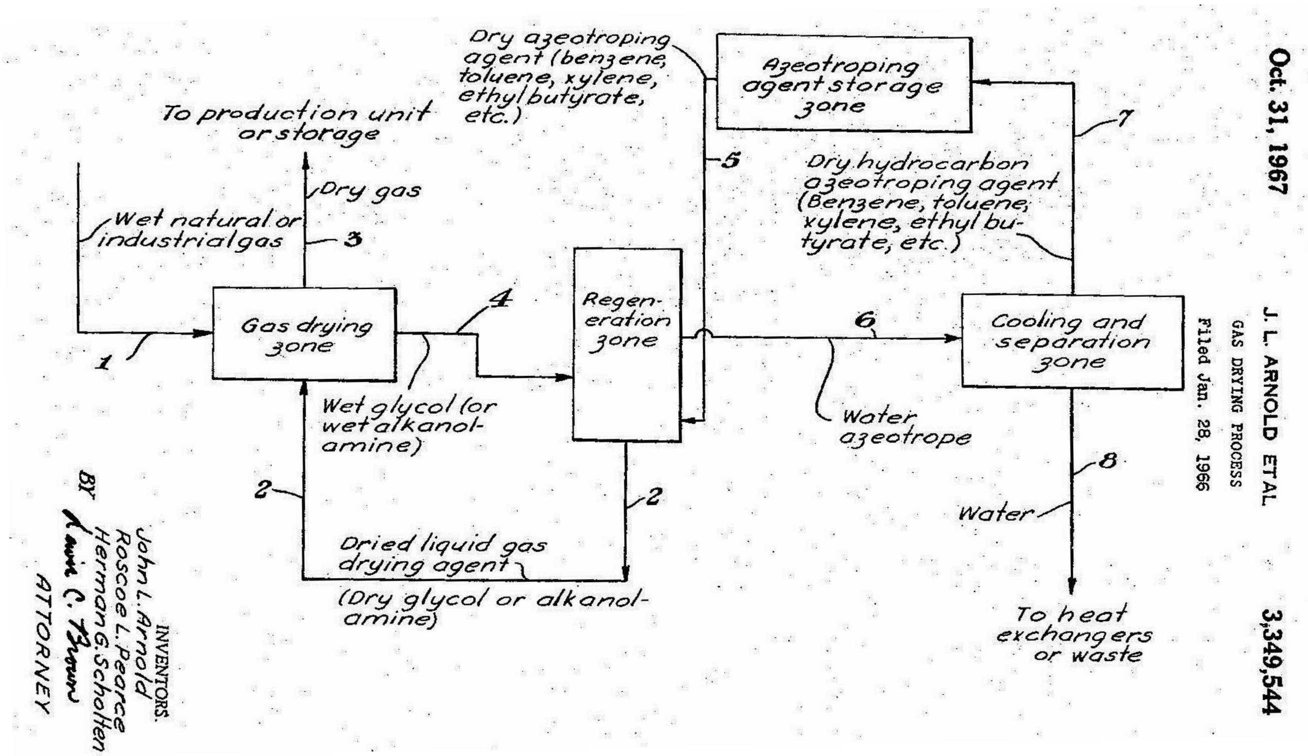


The introduction of a gas stripping column for polishing the glycol after reboiling allowed regeneration systems to attain a glycol purity of 99.9% for a resultant gas water content of under 4 lbs per MMSCF, which was a specification employed in areas with colder climates where hydrate formation and water condensation in pipelines was more problematic.

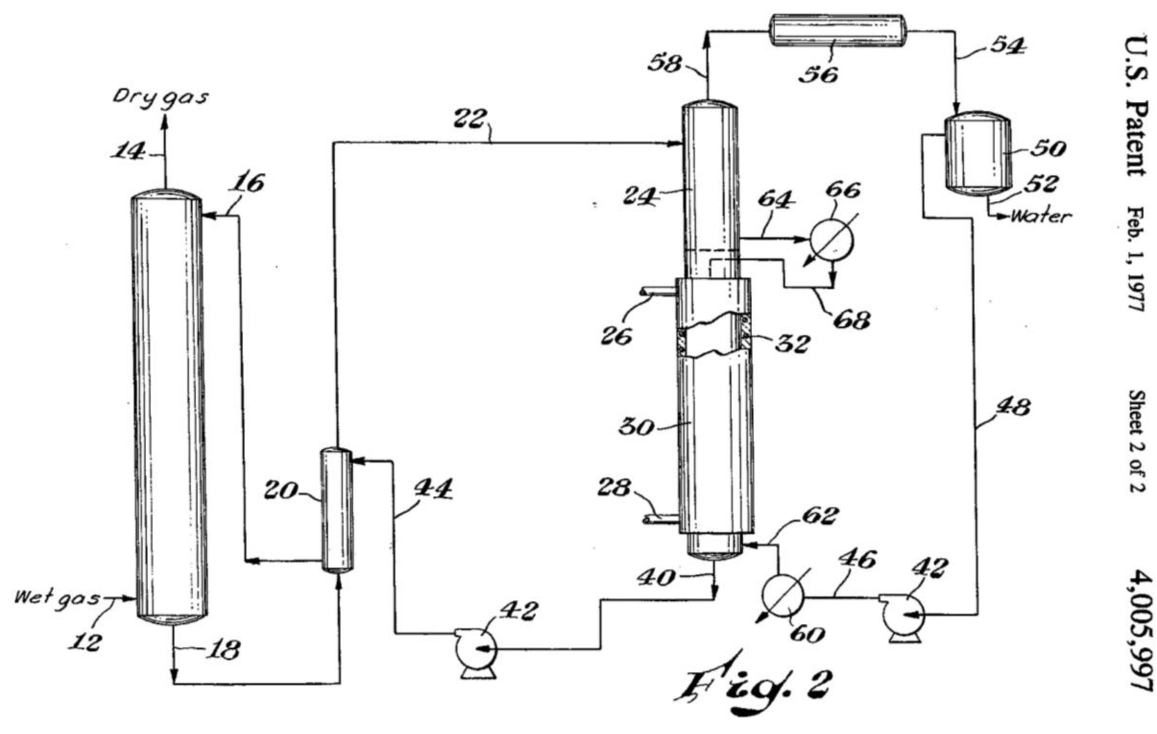
But the main drawback with the Stahl column remains that significant quantities of stripping gas are lost to atmosphere with the reboiler overhead steam.

In 1967 John Arnold, Roscoe Pearce and Herman Scholten of The Dow Chemical Company invented a process of regenerating liquid desiccant by azeotropic distillation (U.S. Patent No. 3,349,544) whereby a condensable hydrocarbon vapor was introduced into the glycol reboiler in order to provide a purer glycol through azeotropic distillation in the reboiler still column.

Still column overheads were condensed and liquid water was rejected while condensed stripping agent was reintroduced to the reboiler. Although the patent dealt with a glycol amine drying and sweetening agent and water dewpoint depressions were not extreme, further patents by Dow exhibited greater gas drying potential.



In 1977 Allan Fowler and John Protz of the Dow Chemical Company invented an azeotropic regeneration process (U.S. Patent No. 4,005,997) that introduced a Stahl-type stripping column downstream of the normal azeotropic glycol regeneration process and condensable hydrocarbon vapor was introduced first into this column for moisture stripping then into the distillation column for primary azeotropic distillation.



Again, the still column overheads were condensed, the liquid water was rejected and the condensed hydrocarbon liquid was pumped, vaporized and reintroduced to the stripping column. This process allowed regeneration systems to attain a glycol purity of 99.99% for a resultant gas water content in the low parts per million.

In 1985 OPC Engineering of Houston acquired the rights to the Dow technology and in 1998 Robert Smith of OPC patented a process using solid desiccant to remove dissolved moisture from the condensed hydrocarbon stripping agent prior to reintroduction to the stripping column of the glycol reboiler (U.S. Patent No. 5,643,421). Glycol purities of 99.999% with a resultant gas water content as low as 0.1 part per million became attainable. This process has been used successfully for gas drying upstream of cryogenic turbo-expander gas plants, but again the total still column overheads are condensed, involving aerial coolers, separators, pumps and drying systems.

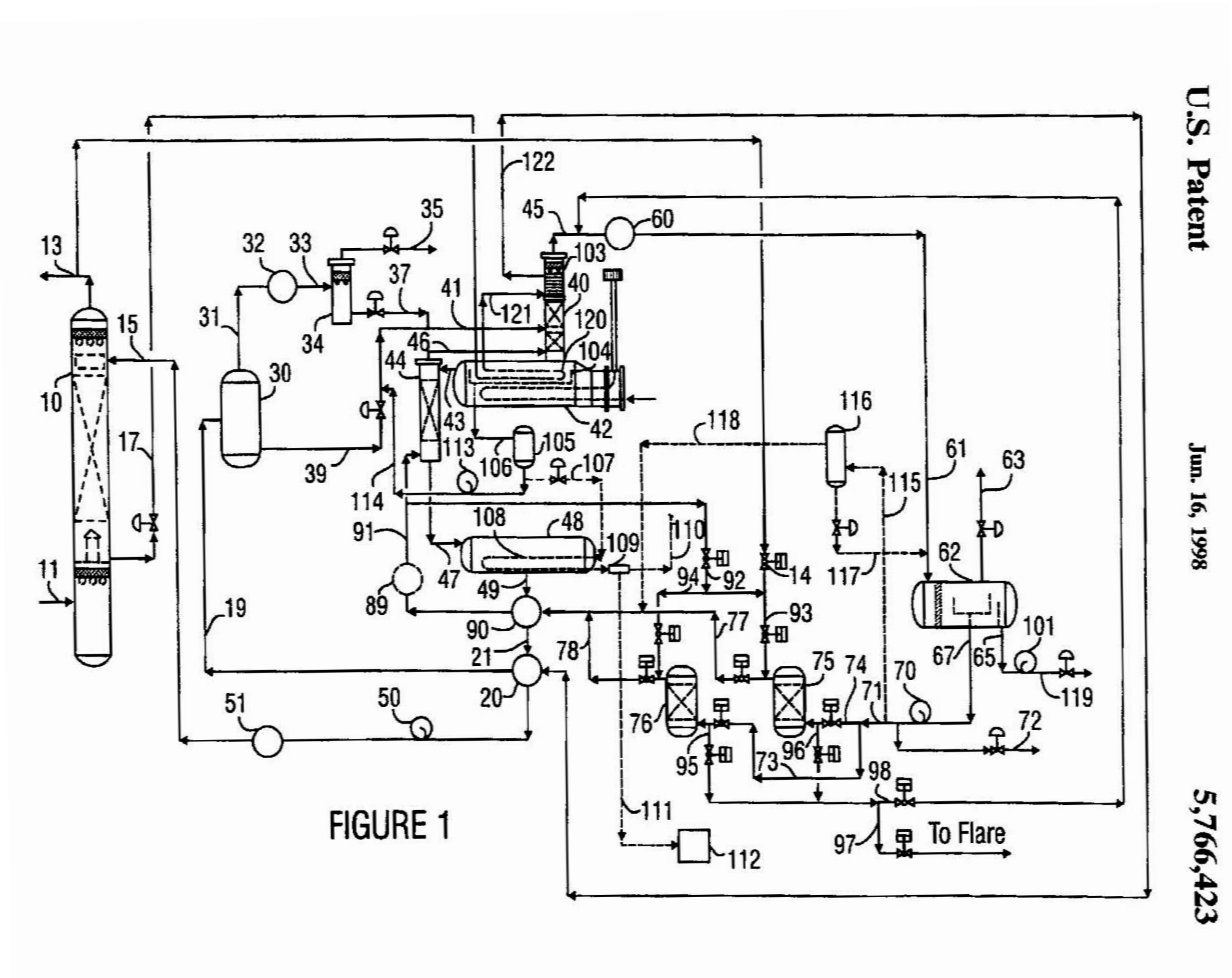


FIGURE 1

In 2005 work began on a modified DOW process whereby an improved and simplified method of azeotropic stripping and distillation of gas drying liquid desiccants was made possible.
A liquid seal was introduced between the glycol reboiler and the polishing stripping column in which a condensable octane vapor counter-currently contacts the semi-lean descending glycol to remove the last traces of water.
The water laden stripping vapor rises up an internal conduit of a separation chamber mounted above the stripping column to an octane condensing coil where the octane stripping medium and water vapors are liquefied and separated.
The stripping octane is then gravity fed to a vaporizing coil in the reboiler for vaporization and reintroduction to the stripping column.

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Seibert (43) **Pub. Date: Feb. 21, 2008**

(54) **METHOD OF DEHYDRATION OF GASES WITH LIQUID DESICCANTS**

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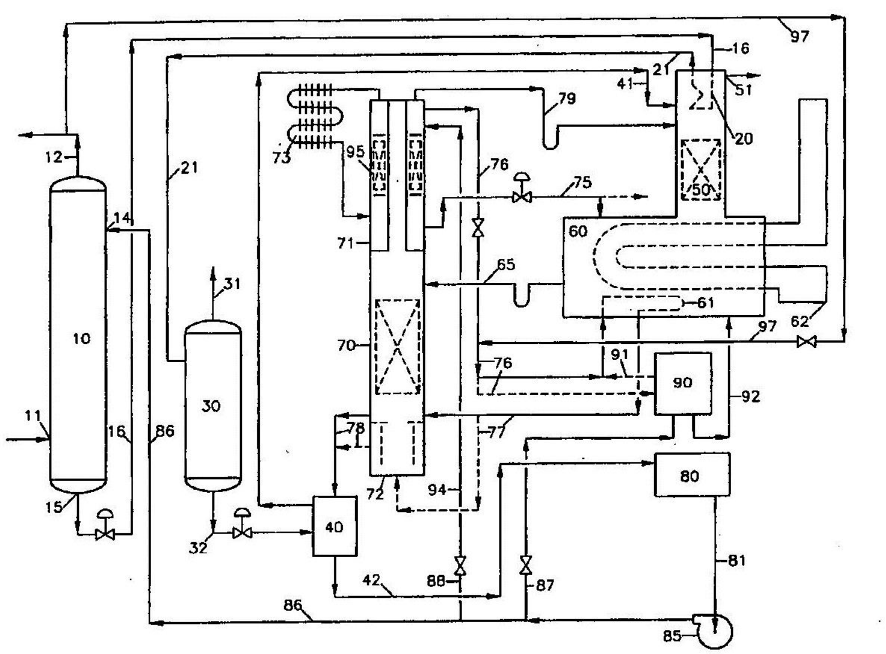
(57) **ABSTRACT**

An improved method of drying natural or other gases to extremely low water dewpoints via countercurrent contact with very pure hygroscopic liquid desiccant which is regenerated by heating and reboiling in a distillation stripping column. Preferably, the liquid desiccant is further regenerated in an azeotropic distillation stripping column using a condensable hygroscopic vapor as a stripping and azeotroping medium.



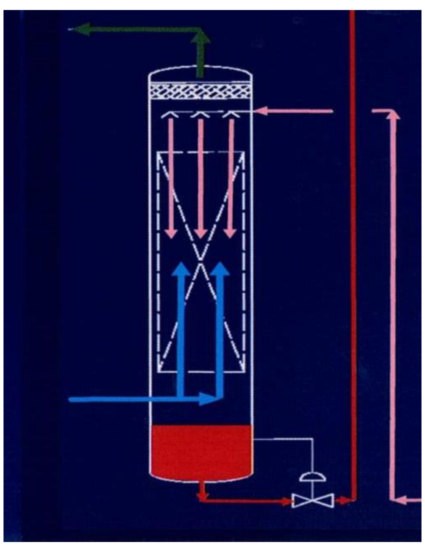
This thermally driven octane recycling percolation system eliminates pumps and simplifies other systems required in the previously described azeotropic processes and eliminates the venting of methane stripping gas that has become so environmentally problematic in the Stahl process.

The STL Azeo Dehy process regenerates a hygroscopic liquid desiccant to a very low moisture content using a condensable octane vapor in a recirculating stripping vapor loop, allowing for the attainment of extremely low water contents of natural gases without the utilization of non-condensable methane stripping gas, which is typically vented to atmosphere. And the process works without condensing the total distillation column steam overheads.

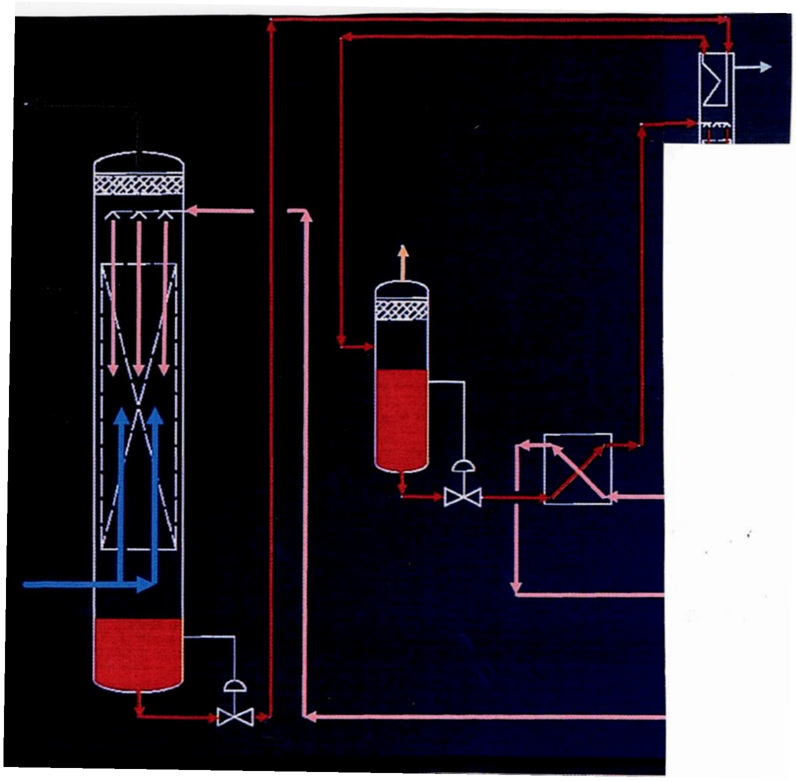
Although this liquid desiccant regeneration system is designed to operate with condensable octane vapor, it may be started up and operated with non-condensable methane stripping gas in the stripping column as operating, process and environmental circumstances warrant. But the use of a condensable hygroscopic octane stripping vapor in lieu of methane stripping gas allows for the elimination of costly stripping gas losses.

The Azeo-Octane Process also allows for improved recovery of desiccant absorbed hydrocarbons such as propane, butane and pentane plus liquids and, in particular, condensable BTEX hydrocarbons such as benzene, toluene, ethyl benzene and xylene. These vaporized liquids and gases are difficult to condense in the presence of methane stripping gas, so the utilization of a condensable stripping medium becomes imperative when recovering desiccant absorbed liquid hydrocarbon products. This is accomplished by condensing the overheads of the reboiler distillation column, consisting mainly of steam but also quantities of condensable hydrocarbons and, in some cases, non-condensable gases and separating same in a three phase separation vessel into water for disposal, hydrocarbon liquids for further processing or sale and non-condensable gases, if present, for thermal oxidation or venting.

THE AZEO-OCTANE GAS DEHYDRATION PROCESS

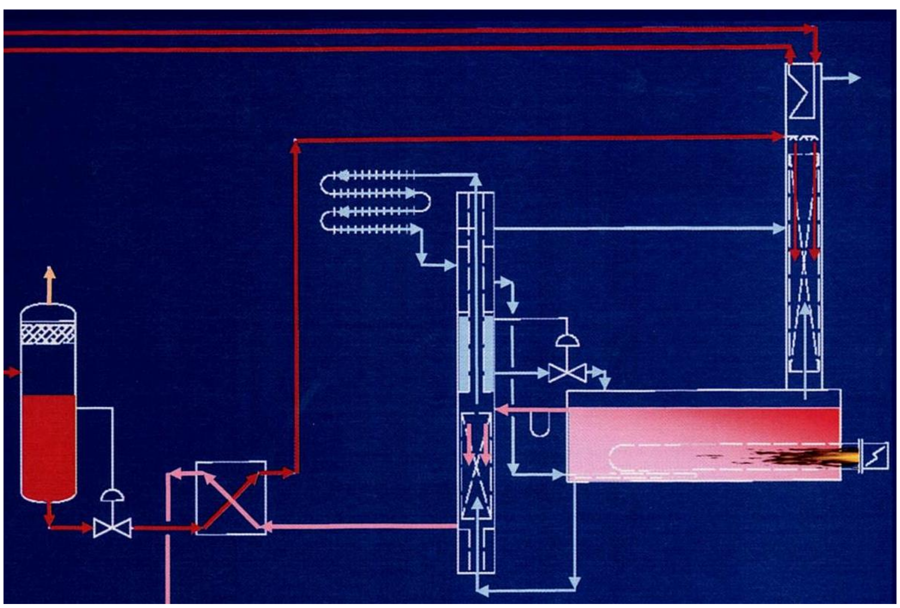


The drying of natural gas takes place in a high pressure gas/glycol countercurrent contactor with the relatively high pressure wet gas entering the bottom of the contactor and the dryed gas exiting the top. Lean or dry glycol enters the upper side of the contactor and rich or wet liquid desiccant exits the bottom of the contactor.



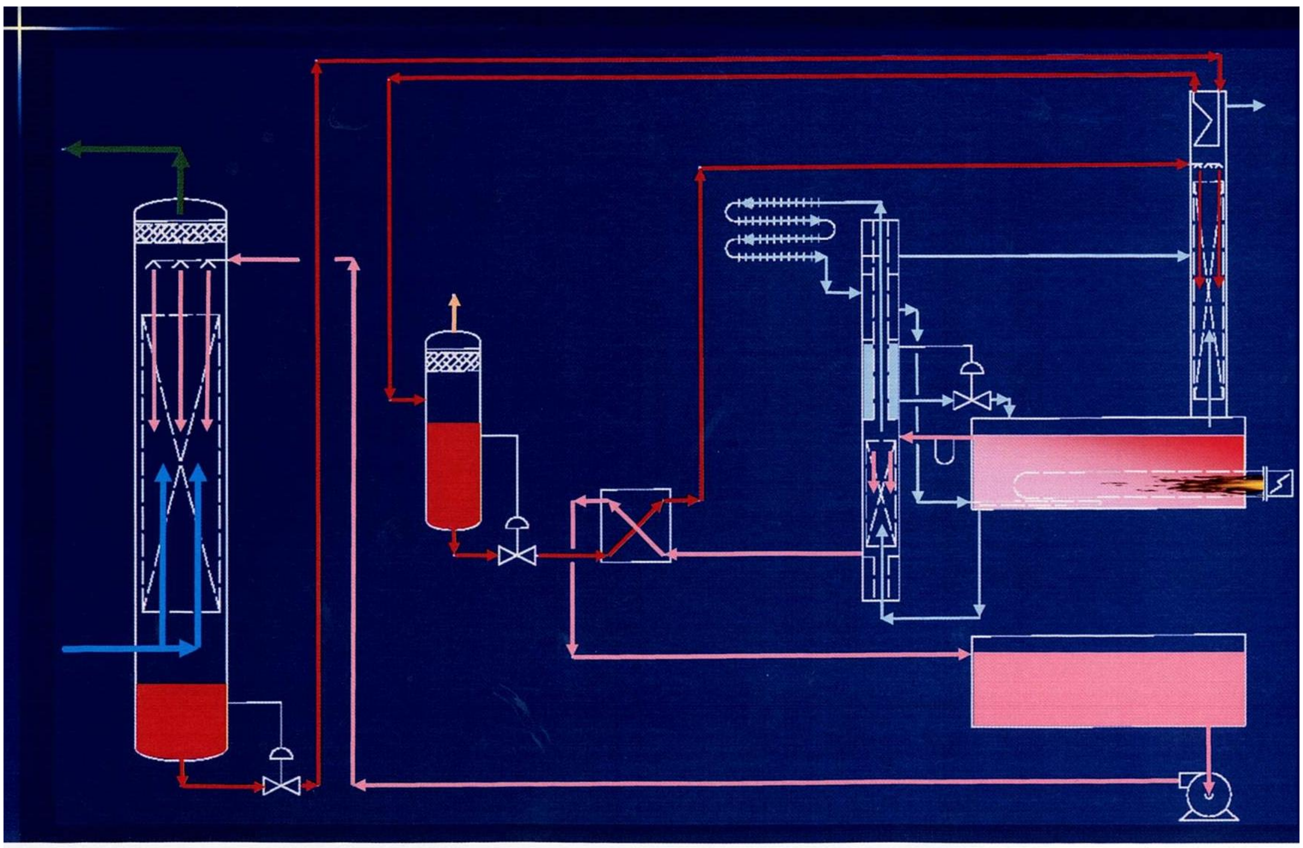
Rich liquid desiccant is level controlled from the contactor to the still column condensing coil of the reboiler, where the cooling effect of the relatively cold liquid desiccant condenses reflux water out of the distillation column overhead steam to minimize overheads glycol vaporization losses, and the now warm rich glycol then flows to the glycol flash separator where absorbed soluble gases are flashed off.

Rich glycol is level controlled from the flash separator to the rich/lean glycol heat exchanger, where rich glycol is heated and lean glycol is cooled, and the now hot rich glycol is directed to the top of the reboiler distillation (still) column, for primary regeneration.



The rich glycol flows down the still column, which is equipped with a packed section, and counter-currently contacts reboiled glycol and water vapors and the heat from said contact strips the water from the downflowing desiccant. The vaporized water rises up the still column and is directed to atmosphere or to a thermal oxidizer or to an overheads condenser for further processing. In the latter case, the condensed steam and any condensed and non-condensed process vapors may be directed to an overheads separator from which the water is directed to a disposal tank, the process liquid, hydrocarbon or otherwise, to a storage tank for reuse as stripping agent or commercial sales, and the non-condensable process gases, hydrocarbon or otherwise, may be directed to a sweetener, an incinerator or to atmosphere as process and environmental conditions warrant.

The now lean glycol exits the bottom of the still column and enters the reboiler, by which heat is added to the process to develop the overhead vapors required in the still column reaction, and the lean glycol is liquid seal or level controlled from said reboiler to the glycol stripping column. The stripping column may be external to the reboiler but is preferably mounted vertically through the reboiler so that the stripping column is immersed in hot liquid desiccant to make up for heat lost in the process of vaporizing further water with hot octane stripping vapor in the stripping column. Heat is generated in the reboiler via a natural gas fueled firetube, an electric heating coil or a heat transfer medium.



The lean glycol enters the top of the liquid desiccant stripping column, which is equipped with a packed section, and flows down, counter-currently contacting rising hygroscopic condensable octane stripping vapors which absorb most of the remaining traces of water in the desiccant, which then exits the bottom of the stripper. The rising moisture laden condensable vapors flow up an annulus of the stripping medium/water separator and are directed to an overheads condensing coil, where the condensable stripping medium and absorbed water vapor are condensed into two immiscible liquids. The condensed liquids enter midpoint into the side of the stripping medium/water separator, and the water gravity settles to the bottom of the separator where it is level controlled back to the reboiler or to a disposal tank, and the liquefied octane rises to the top of the separator where it accumulates and is gravity fed, or pumped, at a set stripping flow rate through the reboiler stripping medium vaporizing coil prior to reintroduction to the stripping column. Excess stripping octane may be drawn off or consumed octane may be made up, from a stripping medium storage tank.

Lean glycol then flows from the stripping column to the lean/rich glycol exchanger, by which it is cooled, and on through to the glycol accumulator. Lean glycol from the accumulator is drawn into the glycol recirculation pump and is reinjected into the top of the gas/glycol countercurrent contactor, thus completing a full regeneration circuit.

BENEFITS OF THE AZEO DEHY PROCESS

Elimination of Stripping Gas Venting

A major benefit of the Azeo Dehy process is the elimination of methane stripping gas losses by using condensable recycling octane stripping medium for enhanced glycol purity. One aspect of the Azeo Dehy process that may find its way into the hearts of gas company operators is the unique ability of the process to be switched from Azeo Octane to Methane Stripping Gas and back again, all while under full operation. This allows a new client to try out the Azeo process without risking capital expenditure because the industry standard Stahl stripping gas process can be reverted to at any time. The original DOW process cannot do this. Also, the ability of the Azeo process to condense the stripping octane without condensing the total steam overheads allows for conventional venting of steam to atmosphere, eliminating the disposal problems associated with octane contaminated water. And the process can be employed at sites where electrical power is unavailable. Again, the original DOW process cannot do this.

Elimination of BTEX Emissions

An additional benefit of eliminating methane stripping gas venting is the improved ability to condense BTEX vapors out of the still column overheads for environmental emission control and profit. If stripping gas is vented to atmosphere any BTEXs in the overheads vent stream go into equilibrium with the methane gas and will not condense at normal atmospheric ambient temperatures.

Extreme Water Dewpoint Depression

MOL

GURGURI GAS FIELD
SNGPL HOURLY PIPELINE OPERATIONS LOG

24 hour period Ending 8:00 PST : 5/23/200 8:00:00 AM

Hourly Averages Summary

Time	Temperature Deg F	Upstream Pressure at PCV15041 psig	Delivery Pressure at PCV15041 psig	Volumetric Flow Rate MMscf/d	Carbon Dioxide mole %	Water Content lbs/MMscf	Hourly Energy MMBTU
0:00	89.00	1,230.00	1,126.00	37.51	2.22	0.06	1,585.16
1:00	89.00	1,230.00	1,129.00	37.50	2.22	0.06	1,586.29
2:00	90.00	1,230.00	1,132.00	37.44	2.22	0.06	1,583.30
3:00	90.00	1,230.00	1,135.00	37.38	2.22	0.06	1,581.90
4:00	89.00	1,230.00	1,137.00	37.48	2.22	0.06	1,585.55
5:00	90.00	1,230.00	1,138.00	37.47	2.22	0.05	1,584.80
6:00	90.00	1,230.00	1,139.00	37.32	2.22	0.05	1,578.30
7:00	90.00	1,230.00	1,137.00	37.35	2.22	0.06	1,580.18
8:00	90.00	1,230.00	1,134.00	37.38	2.22	0.06	1,580.52

0.05 #s/MMSCF

Prepared By Approved By

Shift Incharge Field Manager

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The ability of the Azeo Dehy process to meet extreme water dewpoint depression requirements makes it suitable for gas drying upstream of many cryogenic gas processes, eliminating the need for expensive Mole Sieve processes. In most cases an Azeo Dehy process requires half the Capex and Opex of a Mole Sieve process and is well under half the weight as well.

Modularization

The modularization inherent in the Azeo Dehy design makes for a much smaller footprint than a comparable DOW azeotropic dehydration unit and, of course, several times more compact than a conventional Mole Sieve unit. And the high tech Azeo process, combined with high dewpoint depression Sulzer Structured Packing, is often more compact than a conventional glycol dehydration unit. This saves plant area requirements and reduces off-shore weight support costs.

Another benefit of modularization is reduced shipping costs. Prior South East Asian project shipping costs have been up to 25% of project selling price. By container shipping modularized Azeo Gas Plants, shipping costs below 1% of project price have been achieved.

And shipping times have been more than halved! This can be a deal maker when shops are full and deliveries are tight.

And Some Further Benefits
Some further capabilities of the process include:

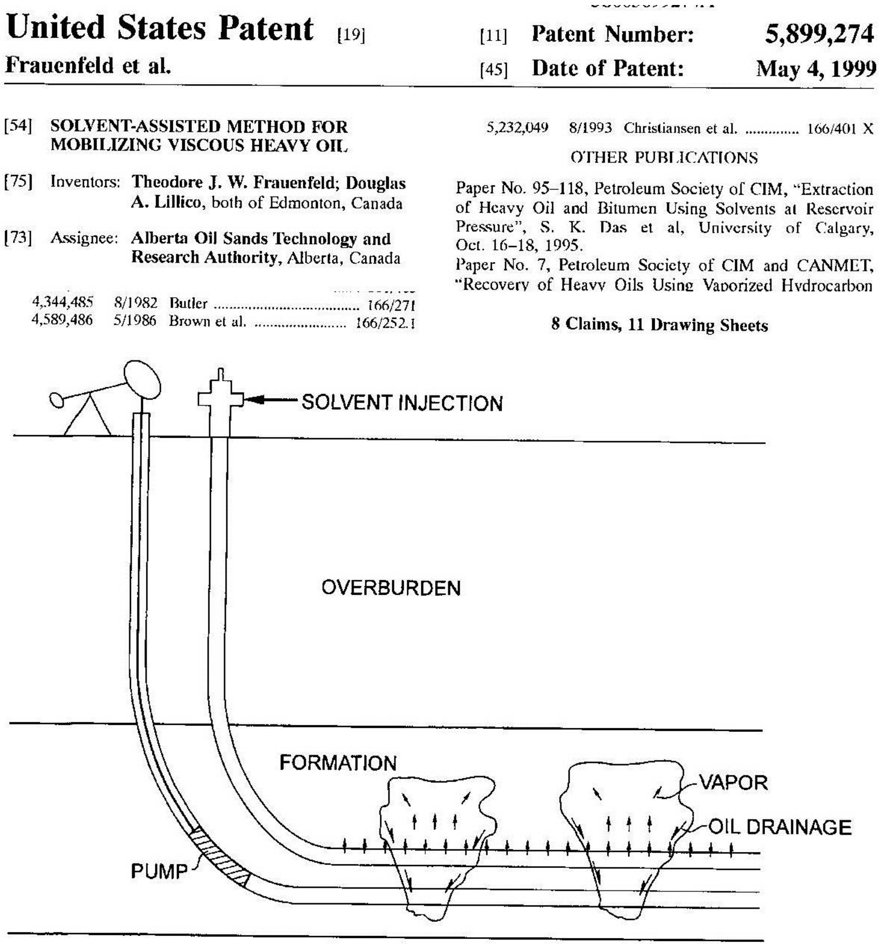
- Operating the reboiler at low pressure for venting into flare systems while maintaining the ability to meet high dewpoint depressions
- Dehydrating gas with MEG in lieu of TEG in order to reduce BTEX and H2S uptake or to eliminate MEG contamination of TEG when upstream MEG injection is employed
- The use of MEA, DEA or MDEA mixtures of amines and glycols as a liquid desiccant for simultaneous drying and sweetening of natural gas
- Ease of operation making the process suitable for remote locations where skilled operators are just not available.

GAS PLANT MODULARIZATION

The use of the Azeo Dehy upstream of LPG Recovery Refrigeration Gas Plants enhances the ability to modularize complete systems up to 150 MMSCFD, allowing for fast track fabrication and installation in remote locations. And the high water dewpoint depression capabilities of the Azeo Dehydration Process allows Turbo-Expander and Post-Choke Refridge Plants to operate in Semi-Cryogenic temperature ranges for up to 50% improvements in liquid recoveries. Up to 100% recovery improvements are attainable with “wild condensates”, liquids that are not fractionated to provide saleable end products.

The Azeo-SAGE Oil Sands Production Process

Recent advances in horizontal well drilling technologies have combined to present an opportunity to utilize the rich shale gas liquids of Northern Alberta and B.C. in the recovery of heavy Athabasca oil sand bitumen using Solvent Aided Gravity Extraction processes. Modularized Azeo Dehy equipped Semi-Cryogenic LPG Refrigeration Plants can be utilized to recover a formulated blend of wild condensates from the rich Montney Shale Gas formations south of Grand Prairie on west to be matched against the particular requirements of in-situ heavy oil solvent recovery processes in the almost continuous oil sands formations from Peace River east to Cold Lake. The depth of LPG "cut" could be matched against the particular in-situ formation depth and characteristics requirements for solvents to be utilized in the Azeo-SEP, SAVEX, VAPEX and other solvent extraction processes.



United States Patent [19]
Frauenfeld et al.

[11] **Patent Number: 5,899,274**
[45] **Date of Patent: May 4, 1999**

[54] **SOLVENT-ASSISTED METHOD FOR MOBILIZING VISCOUS HEAVY OIL**

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[73] Assignee: **Alberta Oil Sands Technology and Research Authority**, Alberta, Canada

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8 Claims, 11 Drawing Sheets

CONCLUSIONS

The Azeo Dehy process offers significant process advantages with high water dewpoint depressions coupled with low environmental emissions as well as greater operating flexibility.

The Azeo Dehy process offers reduced capital expenditure and reduced operating expenditure when compared with other high water dewpoint depression processes.

The Azeo Dehy process offers a reduced footprint and weight savings when compared with other high water dewpoint depression processes.

The Azeo Dehy process offers deep-cut capabilities that can aid in the development of Solvent Aided Gravity Extraction processes used in the recovery of heavy oil.