

## PROCESS FOR THE REMOVAL OF CARBONYL SULFIDE FROM LIQUID PETROLEUM GAS

This application claims the benefit of U.S. Provisional Application No. 60/095,237, filed Aug. 4, 1998.

### FIELD OF THE INVENTION

This invention relates to a method for purifying liquefied petroleum gas. More particularly, this invention relates to a process for the removal of carbonyl sulfide from a liquefied petroleum gas stream utilizing a calixarene as a complexing agent.

### BACKGROUND OF THE INVENTION

Liquefied petroleum gas is an important, versatile hydrocarbon fuel and chemical feedstock. It is commercially available as propane or propane-butane mixtures. It also contains ethane, propylene, isobutane, 1-butene, cis- and trans-2-butene, and n-pentane, in minor concentrations.

Liquefied petroleum gas is generally derived from the refining of crude oil, and as a by-product of the production of natural gas. Products derived from these sources, however, are usually contaminated with impurities such as water, carbon dioxide, and organic sulfur compounds. Such undesirable organic sulfur compounds include, for example, hydrogen sulfide, mercaptans, sulfides and carbonyl sulfides.

Carbonyl sulfide was once considered to be a relatively innocuous contaminant, but is now recognized as being problematic for a variety of reasons. In particular, carbonyl sulfide can hydrolyze in the presence of water to form hydrogen sulfide and carbon dioxide. While carbonyl sulfide is not itself corrosive, the hydrolysis product, hydrogen sulfide, is very corrosive, especially in the presence of water. Consequently, the removal of carbonyl sulfide from liquid petroleum products has become increasingly more important to the petroleum fuel processing industry.

Prior processes commonly used in the refinery industry for removal of carbonyl sulfide from hydrocarbons include (1) treating carbonyl sulfide contaminants with gas plant solutions of an amine, e.g. mono ethanol amine (MEA), diethanol amine (DEA) and other similar amines; (2) hydrolysis of carbonyl sulfide to CO<sub>2</sub> and H<sub>2</sub>S over a catalyst such as activated alumina, platinum sulfide, Co/Mo and other metals; (3) reaction of carbonyl sulfide with a metal oxides such as, for example, ZnO, CuO/ZnO and PbO; (4) adsorption of carbonyl sulfide on a promoted activated alumina or molecular sieves such as 4A, 5A and 13X; and (5) reaction of carbonyl sulfide with potassium hydroxide, sodium hydroxide and/or methanol.

Such processes are, however, disadvantageous for various reasons. For example, carbonyl sulfide reacts rapidly with primary amines such as MEA and DEA to produce salts that can cause equipment fouling. Processes involving hydrolysis of carbonyl sulfide with a catalyst can be complicated and costly since catalyst selection depends on such factors as operating temperature, carbonyl conversion, bed size, estimated life of catalyst, and the like.

Carbonyl sulfide removal with metal oxides is typically not cost effective for most olefin or refinery applications. Metal oxides are sometimes used in the natural gas industry when the concentration of sulfur is very low.

Adsorption processes using molecular sieve products are best for bulk carbonyl sulfide removal at levels of less than 100 ppm where bed outlet levels of 5 ppm are acceptable.

Molecular sieve beds for carbonyl sulfide removal must be very large with short cycles and high regeneration rates. For an olefin unit, E/P feed applications, bed-cycle time and regeneration gas flow requirements are common removal system limits.

Sufnolime™, a solid sodium hydroxide supported on a non-regenerable calcium hydroxide catalyst, has been used in a fixed bed for removal of carbonyl sulfide. Sufnolime™ is microscopic and difficult to remove from the bed. Further, the active catalyst is only 10% to 14% of the catalyst weight; thus, requiring a relatively large bed size.

Potassium hydroxide is more reactive than sodium hydroxide and can remove greater amounts of carbonyl sulfide in liquid/liquid contacting applications. Solid potassium hydroxide beds have also been successful. However, potassium hydroxide can be costly and in some cases, not economically feasible.

Consequently, there exists a need in the petroleum refining industry for simple, economical and efficacious processes for the removal of carbonyl sulfide from hydrocarbons, in particularly, from a liquefied petroleum gas.

Accordingly, it is an advantage of the present invention to provide a process for the removal of carbonyl sulfide from a liquid petroleum gas using a solid complexing agent.

It is also an advantage of the present invention to provide a process for the removal of carbonyl sulfide from a liquid petroleum gas utilizing a calixarene complexing agent.

It is a further advantage of the present invention to provide a process for the selective removal of carbonyl sulfide from liquid petroleum gas stream utilizing a solid calixarene complexing agent.

Additional advantages and objects of the invention will be set forth in part in the description, and in part will be obvious from the description, or may be learned by practice of the invention. Other advantages and objects of this invention may be realized and obtained by means of the process particularly pointed out in the appended claims.

### SUMMARY OF THE INVENTION

We have now discovered that a calixarene selectively reacts with carbonyl sulfide contained in a liquid petroleum gas stream to form a stable complex which can be isolated and removed from the gas stream. The formation of this complex provides the basis for a simple and economical process for the removal of carbonyl sulfide from liquefied petroleum gas.

Accordingly, the method of the present invention comprises contacting a liquefied petroleum gas stream containing carbonyl sulfide as an impurity with a calixarene complexing agent. The liquefied petroleum stream is contacted with the desired calixarene in an amount sufficient to remove all or substantially all of the carbonyl sulfide contained in the petroleum stream.

### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 illustrates a solid-liquid contactor system useful to perform the process of the present invention.

FIG. 2A illustrates a Fourier transform infrared spectrum of carbonyl sulfide.

FIG. 2B illustrates a Fourier transform infrared spectrum of p-t-butylcalix[4]arene complexed with carbonyl sulfide.

FIG. 2C illustrates a Fourier transform infrared spectrum of p-t-butylcalix[4]arene.