

liquid petroleum gas in a liquid state. The temperature will vary depending on the composition of the petroleum gas. In general, however, the temperature is maintained at a range of about 40° C. to about 200° C., preferably about 80° C. to about 150° C.

The pressure of the system is correlated with the temperature range to assure that the petroleum gas is maintained in the liquid state throughout the process. Preferably, the pressure is about 50 to about 500 psig, most preferably about 100 to about 400 psig.

The amount of calixarene complexing agent to be used in the present invention will vary depending on such factors as, for example, the concentration of carbonyl sulfide existing in the liquefied gas stream, the hydrocarbon composition of the gas stream, the particular calixarene complexing agent used, the nature of the contactor system and the contact time, temperature and pressure.

Generally, the amount of calixarene is that amount effective to remove and achieve the desired level of carbonyl sulfide removal. Such amount is easily determined by one skilled in the art through routine experimentation. For example, p-t-butylcalix[4]arene has a carbonyl sulfide uptake factor of 0.41. This means that for every gram of p-t-butylcalix[4]arene that is contacted with carbonyl sulfide contained in a petroleum gas stream, 0.41 grams of carbonyl sulfide will be complexed. In terms of moles, the ratio of carbonyl sulfide to p-t-butylcalix[4]arene is 4.42. Consequently, each p-t-butylcalix[4]arene molecule is capable of complexing 4.4 carbonyl sulfide molecules.

As will be obvious to one skilled in the art, the period of time for intimately contacting the calixarene complexing agent with the crude petroleum gas stream will vary depending upon the amount of carbonyl sulfide desired to be removed. In general, the petroleum stream is contacted with complexing agents from about 0.3 to about 1 minute.

Once the carbonyl sulfide is complexed on the calixarene complexing agent the complex may be isolated from the purified gas stream using conventional separation techniques, such as filtration, decanting, centrifugation and the like. Following isolation, the complex may be gently heated to release carbonyl sulfide and regenerate the complexing agent. In general, the complex is heated at a temperature of about 85° C. to about 150° C. for about 20 minutes to about 2 hours to retrieve the calixarene complexing agent. The retrieved complexing agent may be reused in subsequent carbonyl sulfide removal treatments.

It should be understood that the process of the present invention is not to be limited to the use of the invention as described above, and modifications within the foregoing description can be made while still falling within the spirit of the present invention. For example, it is possible to perform the present invention by simply mixing the calixarene complexing agent with a liquefied petroleum gas containing carbonyl sulfide as an impurity in any suitable mixing tank under conditions sufficient for formation of the carbonyl sulfide/calixarene complex, and thereafter separating the carbonyl sulfide-free gas from the complex.

Other features of the invention will become apparent in view of the following Examples which are given for illustration of the invention and are not intended to be limiting thereof.

EXAMPLE 1

A simple manifold was constructed to allow controlled contact between carbonyl sulfide and p-t-butylcalix[4]arene. Approximately 0.01 grams of p-t-butylcalix[4]arene was placed in a stainless steel fitting in the manifold. The

manifold was pressurized with carbonyl sulfide at 165 psi and allowed to equilibrate for 1 hour. At the end of the hour the manifold was depressurized and the carbonyl sulfide vented.

Subsequent analysis with Fourier transform infrared spectrometry (FTIR), using a potassium bromide pellet formed from the carbonyl sulfide exposed p-t-butylcalix[4]arene revealed that, in fact, a stable complex was formed. Results are recorded in FIG. 2.

As shown in FIG. 2, the major carbonyl sulfide absorption was a packet centered at 2061 cm⁻¹. In the spectrum of the exposed p-t-butylcalix[4]arene, this packet was shifted to 2022 cm⁻¹. This shift in an inclusion complex was not unusual. This carbonyl sulfide/p-t-butylcalix[4]arene peak (at 2022 cm⁻¹) persisted after the pellet was allowed to stand in ambient air overnight, and after the pellet had been reground. This indicated that the complex was very stable.

Temperature dependent measurements indicated that the complex could be disrupted by gentle heating to 85° C. FTIR peak absorbance was monitored as a function of time. Results were recorded in FIG. 3. The decrease in FTIR peak absorbance in FIG. 3 indicated the gradual release of carbonyl sulfide from the complex.

EXAMPLE 2

The procedure of Example 1 was repeated but instead of mixing the exposed p-t-butylcalix[4]arene with potassium bromide for analysis by FTIR, the p-t-butylcalix[4]arene exposed to carbonyl sulfide was placed in a stream of humidified nitrogen. 100% relative humidity nitrogen was passed over the exposed p-t-butylcalix[4]arene at a rate of 1.0 liter per minute for 30 minutes. After exposure to humidified nitrogen, FTIR analysis using a potassium bromide pellet formed from the carbonyl sulfide exposed p-t-butylcalix[4]arene revealed that the carbonyl sulfide was still present in the complex and had not reacted with the water vapor.

EXAMPLE 3

The uptake level of carbonyl sulfide by p-t-butylcalix[4]arene was determined.

76.914 mg of p-t-butylcalix[4]arene was weighed into a boat in a manifold. The boat was exposed to carbonyl sulfide at 165 psi for 1 hour. The boat was removed and placed on an analytical balance to measure the weight loss as a function of time. Results are shown in FIG. 4.

Initially, the mass of the exposed p-t-butylcalix[4]arene was 109 mg which indicates that the capacity for carbonyl sulfide uptake by p-t-butylcalix[4]arene is significant. The uptake factor was determined to be 0.41. This means that for every gram of p-t-butylcalix[4]arene that is exposed, 0.41 grams of carbonyl sulfide is complexed. This is a far higher uptake that would be expected from a simple adsorbent. Over 130 minutes, the uptake factor fell to 0.12 which corresponds to the formation of a 1:1 complex of carbonyl sulfide/p-t-butylcalix[4]arene.

Obviously, numerous modifications and variations of the present invention are possible in light of the above teaching. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described herein.

We claim:

1. A process for the removal of carbonyl sulfide from liquefied petroleum gas stream, which method comprises contacting