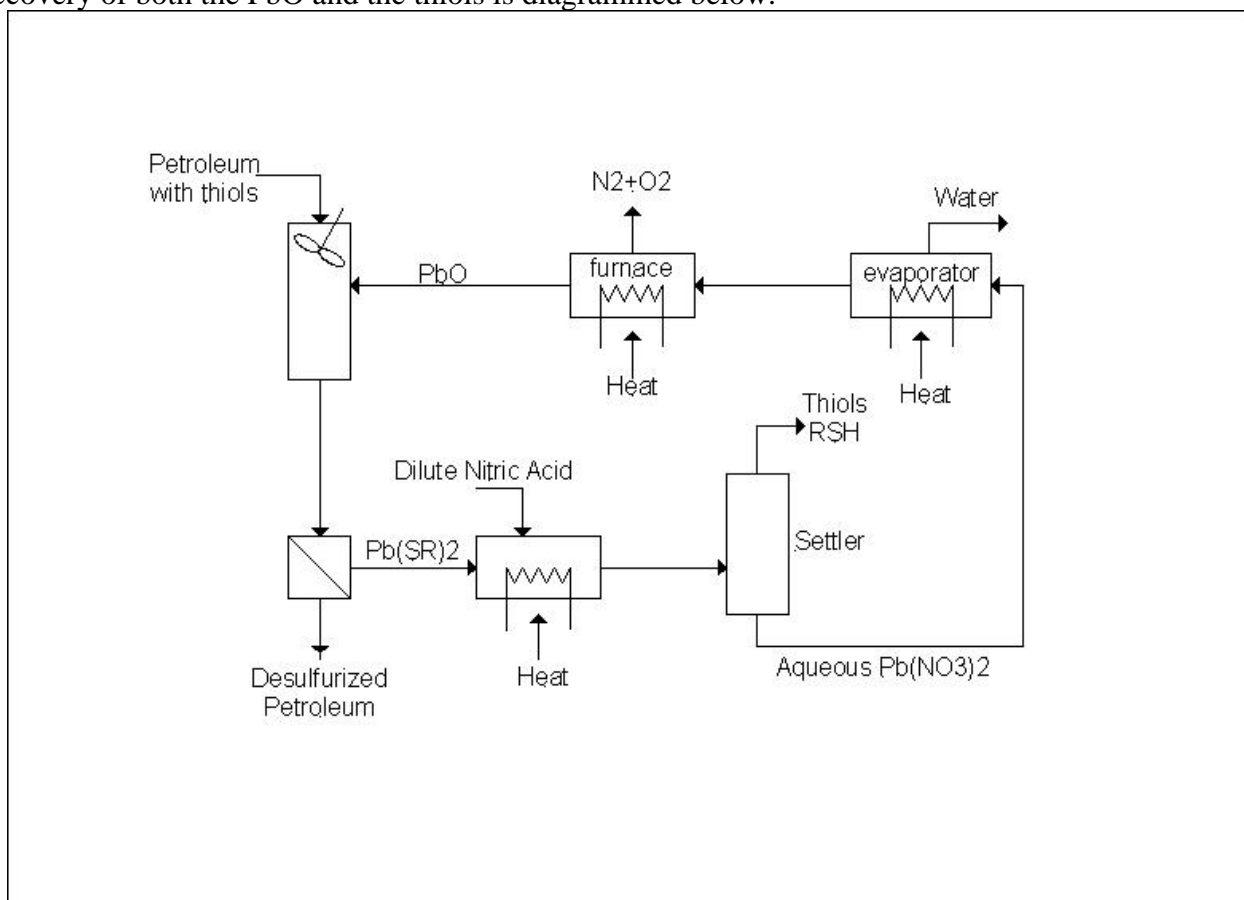


Sulfur Recovery from a Hydrocarbon Stream by a Heterogeneous Reaction with Lead Oxide

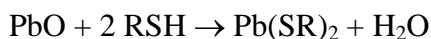
The heterogeneous reaction of thiols with lead oxide to form insoluble lead thiolates is the basis for a new process that separates thiols from a hydrocarbon stream. The process uses inexpensive materials and significantly less energy than conventional hydrodesulfurization (HDS). The process also allows the original thiols to be recovered for other uses, and the Pb is also recovered and recycled. Experimental demonstrations of key stages of the process are presented. Experimental recovery of the Pb for recycling exceeds 94%. Thiols are recovered with typical yields of 80-90%.

Process Description

The complete process for the separation of thiols from hydrocarbons with PbO and the recovery of both the PbO and the thiols is diagrammed below.

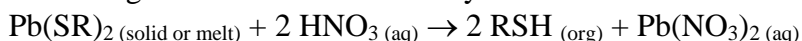


The hydrocarbon stream is contacted with powdered PbO or any other lead oxide in a reactor. The PbO reacts with the thiols to form yellow solid lead thiolates; these thiolates are insoluble in water, acetone, cyclohexane, or toluene at temperatures below about 50°C.



This reaction occurs readily at room temperature. While the reaction can also be performed at an elevated temperature, heating to above 60-80°C causes the thiolates to melt and become miscible in hydrocarbons, preventing their separation. If heated, the reacted stream must first be cooled to near room temperature prior to separation, to ensure that the thiolates have completely recrystallized. The solid thiolates can either be filtered or settled to achieve the desired separation.

Once the thiolates are separated from the hydrocarbon mixture, they can be converted back to the original thiols and a Pb salt by reactive extraction with dilute nitric acid.



The $\text{Pb}(\text{NO}_3)_2$ remains in the aqueous solution while the thiols separate into an organic phase. The reaction can be carried out at room temperature with solid lead thiolates, but the interfacial contacting can be improved by melting the thiolates and forming a miscible solution with an organic solvent.

The compound $\text{Pb}(\text{SC}_8\text{H}_{17})_2$ was found to form a miscible solution with the residual cyclohexane at 54-55°C, so the required operating temperature of the extractor is approximately 60-80°C, depending on the composition of the feed stream.

The two liquid phases, now consisting of an aqueous lead salt solution and a hydrophobic thiol layer, are allowed to settle and are separated. The aqueous layer is separated and evaporated off, leaving solid $\text{Pb}(\text{NO}_3)_2$. Active PbO can be regenerated by roasting $\text{Pb}(\text{NO}_3)_2$ in air, liberating nitrogen and oxygen.

An alternative method for desulfurizing stocks of petroleum fuels is to use this reaction with metallic Pb as the PbO source. Metallic Pb oxidizes rapidly when exposed to humid air. The natural oxide coating on a piece of metallic Pb is also active for this reaction, provided that a supply of oxygen, such as air, is available to regenerate the surface oxide layer. The reactor and separator in Figure 1 could be replaced by rods of Pb placed into storage tanks of thiol-containing petroleum fractions.

Results

The reaction of PbO with excess *n*-octanethiol produced thiolates at room temperature with or without mild agitation. The yield of thiolates, as determined by the change in mass of the solids divided by the theoretical change in mass to convert all PbO into $\text{Pb}(\text{SR})_2$, corrected for water loss, is above 80% on most runs, even at low thiol to PbO molar ratios. The low yield for the 179.5 molar ratio is most likely due to transfer and filtering losses, since this trial used the smallest mass of PbO. Significant reductions in the level of sulfur were achieved in a batch reactor with mild agitation at room temperature.

The limit for the removal of thiols by this reaction can be determined from thermodynamics. The equilibrium constant for this reaction, assuming unit water activity (worst case) is approximately 1.9×10^{21} , permitting the removal of thiols to 23 parts per trillion. The thermodynamic limit of this reaction permits desulfurization to extremely low levels, although kinetic and mass transfer limitations prevent this limit from being practically achieved.

Figure 2 presents a series of photographs demonstrating the reaction of 3 mL *n*-octanethiol diluted with 4 mL cyclohexane with 0.75g PbO_2 at room temperature, without

agitation. PbO_2 was used in the photographs for color contrast purposes, since the massicot form of PbO and the thiolate product are both yellow. PbO_2 is black but reacts to form the same yellow thiolate product. Both compounds react in the same way. The reaction is marked by a rapid growth in apparent solids volume as the liquid thiol is converted into solid thiolate. The color change from the black PbO_2 to the yellow $\text{PbO}(\text{SR})_2$ is also evident. The reaction front is also visible as the thiol, which was injected from the top of the jar, mixes with the oxide. The reaction shown occurred over an elapsed time of 23 min.

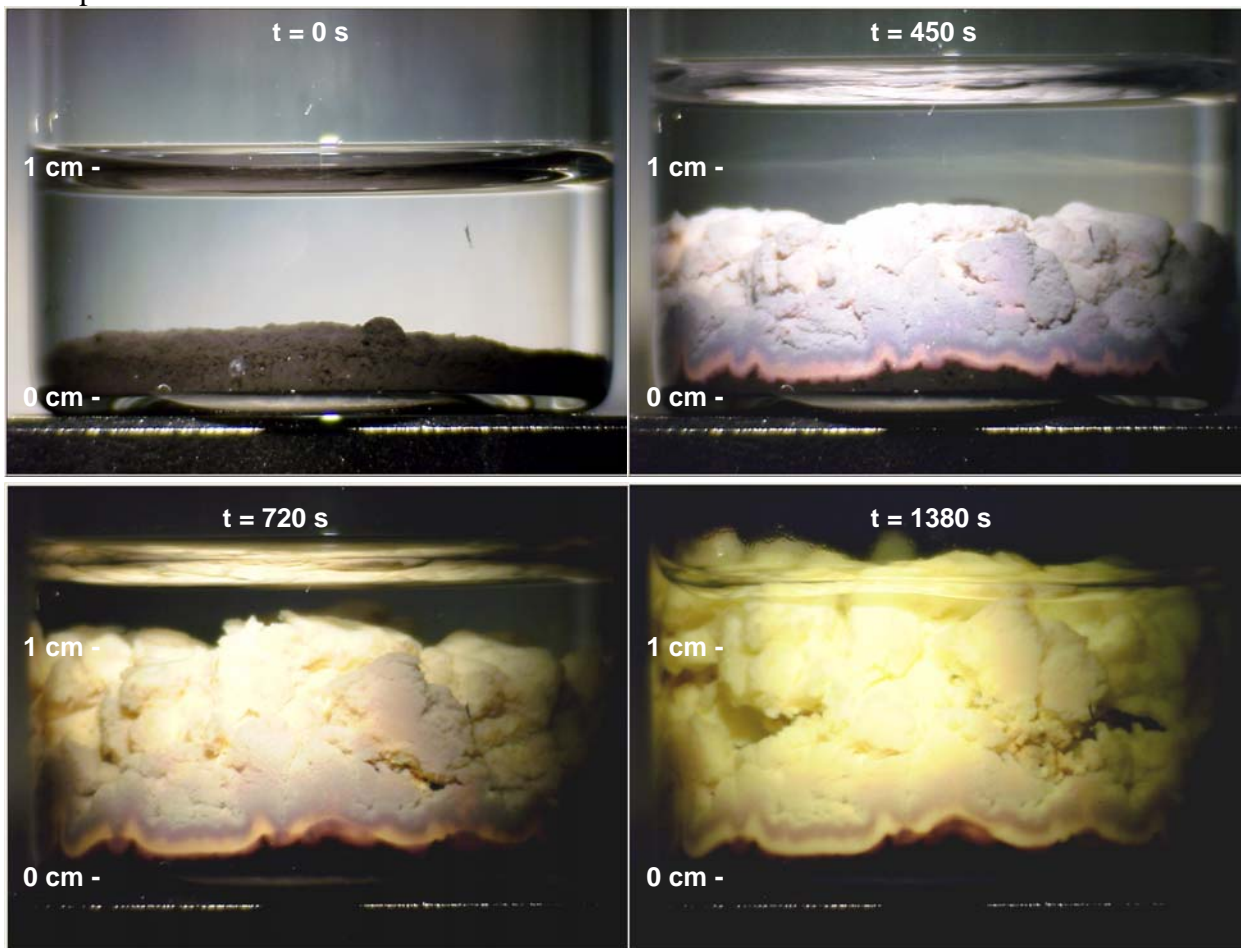


Figure 2. Photographs of the reaction of PbO_2 with *n*-octanethiol. Photographs are chronological, starting from top left, occurring at elapsed times shown. The initial mixture was 0.75 g PbO_2 , 4 mL cyclohexane, and 3 mL *n*-octanethiol (added after first picture).

The reaction of *n*-octanethiol with metallic Pb wire was also successful. An example of this reaction is shown in Figure 3 in which a piece of Pb wire is placed into a liquid consisting of 2 mL cyclohexane and 4 mL of *n*-octanethiol. The reaction is much slower than the reaction with powdered PbO due to the time required for oxygen to diffuse to the Pb surface; the Pb wire also had a lower surface area compared to the powdered oxides.

The reaction shown in the photographs occurred over a period of about 62 hours. The thiolates that were formed on the Pb wire grew in the form of plates which were pushed outwards as new thiolates were produced at the Pb surface.

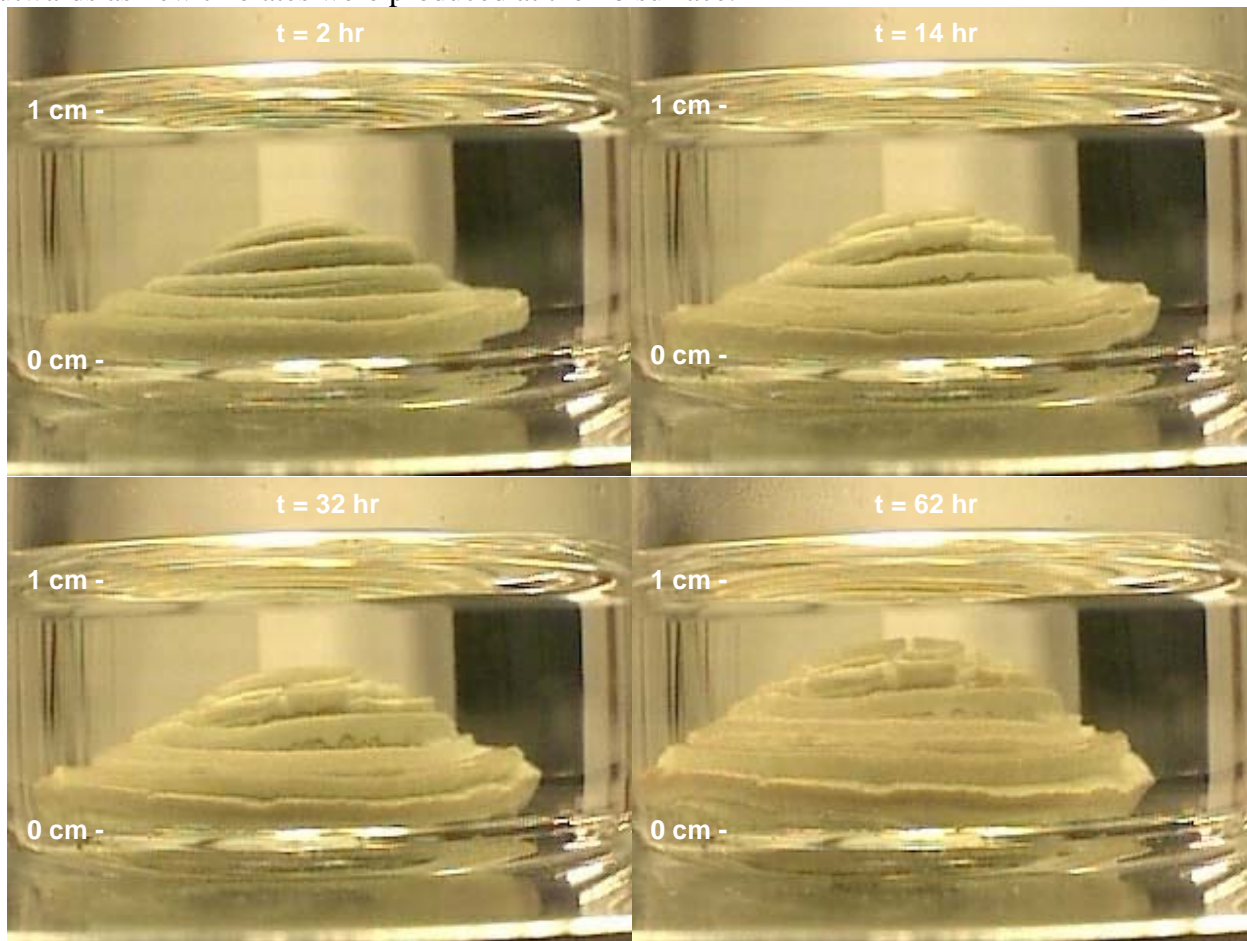


Figure 3. Photographs of the reaction of *n*-octanethiol and metallic Pb wire. Initial conditions are a coil of Pb wire (approx. 8 cm long) in a mixture of 2 mL cyclohexane and 4 mL *n*-octanethiol.

In the extraction studies, the Pb thiolates were successfully decomposed back to the original thiols and $\text{Pb}(\text{NO}_3)_2$ under the experimental conditions. The thiol recovery in the organic phase, as determined by GC, was 78.4%, assuming $\text{Pb}(\text{SR})_2$ as the starting stoichiometry. The recovery of Pb as $\text{Pb}(\text{NO}_3)_2$, as determined by weighing the crystals produced after evaporation of the aqueous phase, was 102%. The slight excess mass is considered experimental error. A second trial using thiolates produced from PbO_2 and using 0.3 M nitric acid yielded a thiol recovery of 90.1% and a Pb recovery of 94.6%.