Low Temperature H₂S Separation Using Membrane Reactor with Redox Catalyst

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CONTRACT INFORMATION

Contract Number
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Period of Performance
October 1, 1992 to September 30, 1994

Schedule and Milestones

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OBJECTIVES

We are combining a low temperature redox catalyst with an H2S selective membrane to create a composite-catalytic-membrane-reactor (CCMR) to help reach pipeline-quality natural gas H2S levels of below 4 ppm. The goal of this program is to identify the apparent kinetic and mass transfer parameters for the CCMR. Using these kinetic and mass transfer parameters a preliminary process design can be made to ascertain the potential of this technology for replacement of conventional amine scrubbing and Claus sulfur recovery processes. In pursuit of this goal the project contains the following activities:

- Construction of reactor and mass transfer equipment suitable for accurate measurements and safe handling of pure H2S.
- Initial proof-of-concept experiments with a prototype CCMR.
- Obtain literature data and develop thermodynamic models for multicomponent natural gas components' solubility in electrolyte solutions.
- Make physical and chemical measurements on the catalyst.
- Obtain kinetic data using a 3-phase slurry reactor.
- Obtain kinetic data for a catalytic membrane under varying mass transfer conditions.
- Develop mathematical models to guide experimental work and for interpretation of results.
- Optimize the permselective membrane part of the CCMR using commercially available materials.
- Further proof-of-concept experiments with an optimized CCMR.
- Develop preliminary process design and economic analysis for the use of a CCMR in gas cleanup.

BACKGROUND INFORMATION

Pipeline-quality natural gas requires H2S levels below 4 ppm. Alternatives to the conventional absorption-stripping and Claus processes are actively being considered. Among these alternatives membrane-based separations seem to have promise. Polymeric membrane processes have already found a niche in CO2 removal and reinjection in the oil field and in the cleanup of natural gas (Spillman, 1989). But it is considered economically infeasible to try to reach 4 ppm H2S in pipeline gas using only a membrane process (Funk and Li, 1990). A potential alternative is a hybrid process (Mckee, et al, 1991 and Pellegrino and Giarratano, 1992). In this case a membrane removes the bulk of the H2S and an amine scrubbing system chemically complexes the remaining H2S to bring the gas stream to pipeline specifications. Ultimately the amine system is regenerated by raising the temperature with steam and stripping the H2S off. All the segregated H2S is sent to a Claus plant where it is eventually converted to elemental sulfur (Kohl & Riesenfeld, 1985). This project proposes another alternative.

We are combining a low temperature redox catalyst with an H2S selective membrane to create a composite-catalytic-membrane-reactor (CCMR). In this membrane reactor the H2S would form a polysulfide on the permeate side of the membrane. The result of this is to eliminate the buildup of H2S in the permeate stream which otherwise decreases the driving force for mass transfer and increases the subsequent membrane area requirements and loss of CH4 in a standard membrane process. The redox reaction occurs in a liquid stream of oxygen-saturated NaOH. Elemental sulfur is recovered by neutralization of the liquid solution with HCl.

The process of creating a mesh with dispersed particles is a general one with several companies having patented products based on such a technology. The process for creating the particulate mesh membrane yields a microporous membrane, which would be unsuitable for doing gas separations. What it is suitable for is creating a very open network of unaggregated particles which would maximize their mass transfer accessibility. It also allows the particles to be easily handled and put into a variety of novel configurations. We will
refer to this mesh membrane, with particles, as the "CAT" membrane.

A variety of liquid phase redox processes for H2S oxidation are known and described in Kohl & Riesenfeld, Meyer et al. and Dalrymple et al.. None of them use a catalytic membrane reactor. In our approach we envision the CAT membrane coated with a thin film of an H2S permeable gas separation membrane. Of particular interest to us is the use of the polyperfluorosulfonic acid (PFSA) polymer with which we have many years of experience and seems especially suitable for this application due to its inherent chemical inertness. We will refer to this PFSA-coated, CAT membrane as a composite catalytic membrane reactor (CCMR).

Prior work by our group has shown that liquid membrane/facilitated transport with ion exchange membranes can achieve very high selectivity for the removal of CO2 and H2S from mixtures containing H2, CO, CH4 and higher hydrocarbons at ambient temperatures. We refer to these membranes as enhanced transport, ion-exchange membranes or ET-IEX. The productivity of the ET-IEX membranes, on a per unit thickness basis, can be greater than or equivalent to the best of the passive membranes and more selective.

We also developed a heat-treatment solvent-swelling approach which dramatically increased the productivity of the membranes (Pellegrino et al., 1988 and Heaney and Pellegrino, 1989). Not only did the permeance of the membranes increase dramatically but so did the permeability. Further experiments with ternary mixtures of H2, CO2 and H2S, using a variety of chemical carriers indicated that larger carriers could effectively be used to vary selectively between H2S and CO2 (Pellegrino et al., 1990). This experience will be drawn upon to maximize the selectivity of the permselective membrane for H2S in the CCMR.

A CCMR offers several potential advantages versus the conventional liquid redox systems. These include: 1) contacting the catalyst with an enriched H2S reactant, 2) segregation of the O2 from the natural gas stream, 3) improved and consistent mass transfer area, 4) lower liquid circulation rates, and 5) compact operation amenable to small-scale operations. Of course the key to achieving any advantages lies in the kinetic properties of the catalyst and how well the reaction kinetics can be matched to the permeation of H2S through the permselective layer. Additionally we need to consider the effect of other permeants on the catalyst's lifetime and activity.

General Description of the Catalyst and H2S Oxidation Reaction

The catalyst is formed with specific surface areas which vary from 5 to 1200 m2/g. The catalyst is perceived to operate due to specific chemisorption with the catalytic oxidation promoted by delocalized electrons.

The overall reaction and stoichiometry can be expressed as:

\[(2n+1)\text{H}_2\text{S} + n\text{O}_2 + 2\text{NaOH} \rightarrow \text{NaS}_2n+1\text{Na} + 2(n+1)\text{H}_2\text{O}\]

and the elemental sulfur is generated from solution by neutralization according to:

\[\text{NaS}_2n+1\text{Na} + 2\text{HCl} \rightarrow 2n\text{S} + \text{H}_2\text{S} + 2\text{NaCl}\]

The following mechanism has been reported as being a likely route to the overall oxidation process (note, C designates the catalyst's active surface sites):

\[\text{C} + \text{O}_2 \rightarrow \text{O}_2 \cdot \text{C}\]

\[\text{O}_2 \cdot \text{C} + 4\text{HS}^- + 2\text{H}_2\text{O} \rightarrow \]

\[\text{C} + 4\text{HS}^- + 4\text{OH}^-\]

\[4\text{HS}^- \rightarrow 2\text{HSSH}\]

\[2\text{OH}^- + 2\text{HSSH} \rightarrow 2\cdot\text{SSH} + 2\text{H}_2\text{O}\]

\[\text{O}_2 \cdot \text{C} + 2\cdot\text{S}_x\text{H} \rightarrow \]

\[\text{C} + 4\cdot\text{S}_x^- + 2\text{H}_2\text{O}\]
\[ \cdot S_x\ +\ \cdot S_y\ \rightarrow\ \cdot S_x\ S_y\ ]

Presumably the catalytic conversion involves sorption of dissolved oxygen at the active sites of the catalyst. Deprotonated H$_2$S in the aqueous NaOH solution forms free radicals with access to the oxidized sites. The free radicals can then combine and form oligomers which in turn become deprotonated and continue the process. The termination groups become the Na salts as the hydroxyl groups become consumed leading to a solution of sodium polysulfide. The neutralization step with HCl frees one H$_2$S per polysulfide and generates a brine solution.

Description of the CCMR Concept

![Diagram of CCMR Concept]

Figure 1 presents a schematic of the composite membrane and the main components of the streams. The sour natural gas flows on the feed (high pressure) side of the module. The aqueous (aq) O$_2$/NaOH stream flows on the permeate side, ideally in a countercurrent fashion. (In plant-scale hardware countercurrent flow may not be plausible.) By controlling the permeation properties of the permselective layer the H$_2$S (and possibly CO$_2$) is the primary component permeating into the catalyst layer. Some of all the other components will also permeate but their fluxes should be small with respect to the acid gases.

The oxygenated NaOH (aq) penetrates into the CAT layer because the latter is a very open

mesh. The oxygen activates the sites on the catalyst and the NaOH promotes the formation of HS free radicals from the H$_2$S that is continuously permeating into the liquid phase. The reaction can proceed as described previously.

The formation of the polysulfide effectively creates a continuous "sink" for H$_2$S. Thus its permeation rate, even when its partial pressure in the feed stream becomes very low, is never completely inhibited. If the rate of reaction and the mass transfer of HS free radicals in the liquid phase are both fast enough with respect to the diffusion rate of H$_2$S in the permselective layer, then there will always be a non-zero driving force for H$_2$S permeation through the membrane.
PROJECT DESCRIPTION

The project is intended to identify the apparent kinetic and mass transfer parameters for a composite-catalytic-membrane-reactor (CCMR). Using these kinetic and mass transfer parameters a preliminary process design can be made to ascertain the potential of this technology for replacement of conventional amine scrubbing and Claus sulfur recovery processes.

Develop a model to describe the composite-catalytic-membrane-reactor.

The model will initially be a 2 dimensional steady state one. The previous Figure 1 can now be taken to represent a differential element. The mass transfer perpendicular to the bulk gas stream will include 4 layers:

- a gas phase mass transfer resistance,
- diffusion through the membrane using a solution-diffusion model,
- a reaction zone with volume averaged properties based on the catalyst loading and porosity, and
- a liquid film resistance.

Note that the gradients will be in opposite directions for many of the components and the species conservation equations will be coupled primarily through the reaction term. The exact form of the reaction term will be modified depending on the results of the batch kinetic experiments. This model is not particularly new and prior work in the literature will simplify its development. We will primarily rely on semi-analytical numerical solutions to exercise the model.

Develop initial kinetic and thermodynamic data.

In order to accomplish this objective we will:

- Construct an experimental apparatus suitable for obtaining apparent kinetic and mass transfer data for the semi-batch oxidation of H\(_2\)S using the catalyst.
- Obtain data for room temperature kinetics.
- Develop a thermodynamically-consistent model for predicting multicomponent gas solubilities in aqueous electrolyte solutions.

Prepare a CCMR and obtain preliminary data.

We will prepare a permselective layer of polyperfluorosulfonic acid (PFSA), or a suitable alternative, on the CAT layer and run experiments using synthetic natural gas feed compositions where gases are permeating through the permselective layer.

We will try to determine the apparent rate limiting steps between membrane permeation, liquid phase mass transfer (including H\(_2\)S, NaOH and O\(_2\)) and surface reaction. For this we will rely on data obtained in the slurry reactor studies.

We will also determine effects of pressure, temperature, pH and liquid phase composition over a limited range of values.

Prepare a Preliminary Process Design

We will use the model to evaluate a membrane process for H\(_2\)S removal from a natural gas stream. The membrane process will be compared to a conventional design obtained from the literature and/or developed with a flowsheet simulator.

RESULTS

Construction of Equipment

We have completed assembly of a flow system suitable for safe experimentation with pure H\(_2\)S streams, as well as CH\(_4\) and other components of natural gas. The system will be used for:

1) measurement of apparent H\(_2\)S oxidation kinetics for a 3-phase slurry reactor in both batch and continuous flow modes;

2) measurement of apparent H\(_2\)S oxidation kinetics for a spinning disk reactor in both batch and continuous flow modes;

3) measurement of gas solubility in aqueous electrolyte solutions, and
4) measurements of permeation and reaction of synthetic natural gas streams in a membrane reactor test module.

The 3-phase slurry reactor will be used to develop a global rate model including effects of $\text{PH}_2\text{S}$, $\text{PO}_2$, $\text{T}$, $\text{pH}$, and ionic composition. The spinning disk reactor, depicted in Figure 2, will enable us to develop mass transfer correlations useful for modifying the rate model. The stirrer speed can be varied and the effects of external film mass transfer into the catalyst mesh layer can be quantified.

![Figure 2. Schematic of Spinning Disk Reactor](image)

**Initial Proof-of-Concept Experiments**

We performed four initial experiments using a catalyst mesh layer containing ~80% solids. This mesh was pressed into a polyperfluorosulfonate membrane ($\text{Na}^+$ form) and mounted into a test cell as indicated in Figure 3. The experiments were performed at 296 K and 221 kPa (20 psig) and the results are listed in Table 1. The precipitate from the first experiment was analyzed using direct insertion mass spectrometry and found to be at least 99.999% sulfur. The sulfur productivity was based on the amount of elemental sulfur precipitated out of the recirculating NaOH stream. This sulfur productivity was similar to what we would expect for $\text{H}_2\text{S}$ permeation through the membrane alone. This leads us to conclude that in these initial experiments the transport through the comparatively thick membrane film was the rate limiting step.

**Physical-Chemical Measurements on the Catalyst**

Several measurements using temperature-programmed desorption were performed which indicated that there was only physical sorption of CO, CO$_2$ and H$_2$O on the catalyst. An indication of the available reaction sites was estimated by the adsorptive capacity for several polar organic compounds: methanol - 1750 $\mu$mol/g, ethanol - 835 $\mu$mol/g, and formic acid - 1656 $\mu$mol/g. The surface area is estimated at $>1000$ m$^2$/g.

**Table 1. Initial Results for Flow Experiments using CCMR Catalyst**

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<tr>
<th>$\text{N}_2$ (%)</th>
<th>Gas Composition (vol %)</th>
<th>$\text{CH}_4$</th>
<th>$\text{CO}_2$</th>
<th>$\text{H}_2\text{S}$</th>
<th>$\text{NaOH}$ (N)</th>
<th>Time (min)</th>
<th>$\text{Sulfur Productivity} \times 10^{10}$ mol/cm$^2$ * s</th>
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Table 2. Approach for Determining Phase Equilibrium

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<td>P, T</td>
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<td>Y_H₂S; Y_O₂; Y_CH₄</td>
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<td>Dissociation constants H₂S, NaOH, H₂O</td>
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HKF - (Helgeson, Kirkham and Flowers, 1981)
EOS - equation of state
Multicomponent Solubility Data and Models

Table 2 summarizes the approach for determining the liquid phase activities of the gaseous feed components and other key reactants during the kinetics experiments. We have determined sufficient data in the literature so that only those measurements which are directly performed during an experiment (i.e., pressure, temperature, pH, etc.) are needed. A computer program is currently being written to implement the thermodynamic model.

A numerical model is being written to implement the schematic problem depicted in Figure 4. It is an ideal case which assumes that a first order reaction occurs through the liquid phase. In using this model we are lumping many real, physical parameters into some pseudo-parameters, which include the partition coefficients of the gas phase constituents, $H_i$, the presumed velocity profile, $V_z$, and the overall reaction rate parameter, $k$. We are taking this approach initially because it may allow us to develop a semi-analytical solution that will be easier to use to explore the effects of changes in parameter values. The model will integrate the material balance of the gas and liquid phases in the $z$-direction and will be useful for design problems.

Nondimensional Parameters

$C = H_i \hat{C}/P_i$  \hspace{1cm} $y = \hat{y}/\delta$  \hspace{1cm} $z = \hat{z}/\delta$  \hspace{1cm} $Pe = v_o \delta / D$

$\frac{\partial^2 C}{\partial y^2} = v_z \frac{\partial C}{\partial z} - \dot{r}$

where $\alpha^2 = k\delta^2 / D$

$k = 1^{st}$ order dimensional rate constant

$\dot{r} = - \alpha^2 C$

Figure 4. Schematic of Simple Model for the Integrated CCMR Performance
FUTURE WORK

Most of our experimental work is still ahead of us. We will perform the 3-phase slurry and spinning disk reactor measurements and complete the modeling efforts. Additionally we will try to optimize a permselective membrane layer to minimize CO₂ permeation. CO₂ reacts with NaOH to form carbonates which will unnecessarily use up reagent. Upon completion of the reactor work and modeling we will perform optimized proof-of-concept experiments and develop a preliminary process design critique.

REFERENCES


END

4/16/94

FILED

DATE