

**Investigation on Durability and Reactivity of  
Promising Metal Oxide Sorbents During  
Sulfidation and Regeneration**

**Quarterly Report  
January - March 1995**

K.C. Kwon

March 1995

Work Performed Under Contract No.: DE-FG21-94MC31206

For  
U.S. Department of Energy  
Office of Fossil Energy  
Morgantown Energy Technology Center  
Morgantown, West Virginia

**MASTER**

By  
Tuskegee University  
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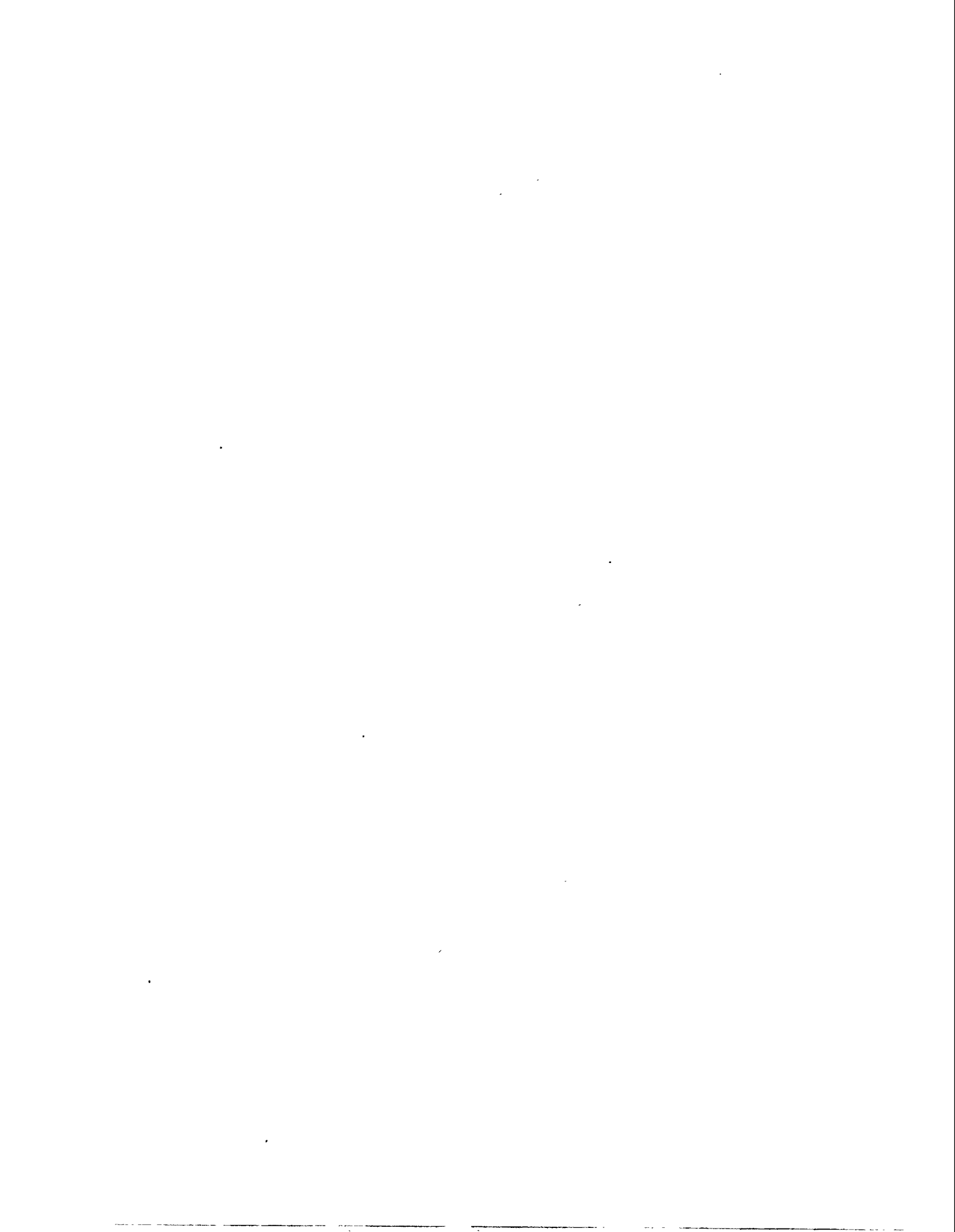
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## ABSTRACT

Hot-gas desulfurization for the integrated gasification combined cycle (IGCC) process has been investigated by many researchers to remove effectively hydrogen sulfide with various metal oxide sorbents at high pressures and high temperatures. Metal oxides such as zinc titanate oxides, zinc ferrite oxide, copper oxide, manganese oxide and calcium oxide, were found to be promising sorbents in comparison with other removal methods such as membrane separations and reactive membrane separations. Some metal oxide sorbents exhibited the quite favorable performance in terms of attrition resistance and sulfur capacity. Removal reaction of  $H_2S$  from coal gas mixtures with ZT-4 or other promising sorbents of fine solid particles, and regeneration reaction of sulfur-loaded sorbents will be carried on in a batch reactor or a continuous differential reactor.

The objectives of this research project are to find intrinsic initial reaction kinetics for the metal oxide-hydrogen sulfide heterogeneous reaction system, to obtain effects of concentrations of coal gas components such as hydrogen, carbon monoxide, carbon dioxide, oxygen, nitrogen and moisture on equilibrium reaction rate constants of the reaction system at various reaction temperatures and pressures, to identify regeneration kinetics of sulfur-loaded metal oxide sorbents, and to formulate promising metal oxide sorbents for the removal of sulfur from coal gas mixtures. Promising durable metal oxide sorbents of high-sulfur-absorbing capacity will be formulated by mixing active metal oxide powders with inert metal oxide powders and calcining these powder mixtures, or impregnating active metal oxide sorbents on supporting metal oxide matrixes.

The Research Triangle Institute, a sub-contractor of this research project, will also prepare promising metal oxide sorbents for this research project, plan experiments on removal of sulfur compounds from coal gases with metal oxide sorbents as well as regeneration of sulfur-loaded metal oxide sorbents, and review experimental results.

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## INTRODUCTION

Coal is the most plentiful energy resource in the United States and continues to be the major fuel utilized by electrical power plants. The coal resources will become more attractive for chemical feedstocks as well as sources of liquid and gaseous fuels, as petroleum resources become more depleted.

Coal is a very complex and heterogeneous material. Effective utilization of coal requires an understanding of the formation, structure, and purification of coal. Raw coal consists of minerals and organic matter. Coal minerals include primarily pyrites, silicate (quartz, clays) and various minor minerals, whereas organic matter is composed of carbon, oxygen, hydrogen, nitrogen and sulfur. Sulfur in coal is present as organic sulfur, pyritic sulfur and sulfate sulfur. Sulfur occurring in the form of relative coarse pyrite particles is removed largely by density separation, but very finely disseminated pyrite and organic sulfur cannot be removed in this way. Sulfur products in combustion not only pollute the environment, but also are detrimental to combustion systems because of the corrosive action of their combustion products. In gasification process, coal is reacted with steam and air or oxygen to produce a medium to high calorific value fuel gas. The fuel gas can be subsequently combusted in a gas/steam turbine combined cycle (IGCC). These IGCC-based power generation options offer much higher thermodynamic cycle efficiencies that promise to reduce all forms of pollutants released from a coal conversion process through a lower fuel consumption and from the use of more energy efficient high pressure and/or temperature unit operations for the removal of environmental pollutants. Among these options, integrated gasification combined cycles (IGCC) are relatively well developed.

Sulfur products in combustion of sulfur present in coal not only pollute the environment, but also are detrimental to combustion systems because of the corrosive action of their combustion products. Removal of hydrogen sulfide from hot coal gas produced in integrated gasification combined cycle power generation systems by metal oxide sorbents is required to protect downstream combustion turbines from being corroded with sulfur compounds. Removal of sulfur compound from coal gas products are investigated by using various metal oxide sorbents, and membrane separation methods. Current research results show that removal of sulfur with metal oxide sorbents appear to be the most promising method among others.

Main requirements of these metal oxide sorbents are durability and high sulfur-loading capacity during absorption-regeneration cycles. Spalling of sulfur-loaded fixed-bed metal oxide sorbents occurs during the regeneration of sulfur-loaded metal sorbents. The main causes of spalling of sorbents appear to be temperature rises of sulfur-loaded sorbents due to tremendous exothermic heat of reaction, and sulfate formation during regeneration processes. Sulfate products occupy more space than sulfide products in pores of sorbents, and result in significant structural stresses of metal sorbents.

The main objectives of this research proposal are to formulate durable metal oxide sorbents of high-sulfur-absorbing capacity by the physical mixing method or the impregnation method, to investigate reaction kinetics on the removal of sulfur compounds from coal gases at high temperatures and high pressures, and to study kinetics on regeneration of sulfided sorbents, using formulated promising metal oxide solid sorbents.

## STATEMENTS OF RESEARCH OBJECTIVES

Experiments will be conducted in an isothermal stirred micro batch reactor or an isothermal continuous differential reactor to obtain kinetic data on both sulfidation of metal oxide sorbents and regeneration of sulfided metal oxide sorbents, and experimental data on mechanical/thermal stabilities of formulated metal oxide sorbents suitable for the design of bench-scale/pilot-scale transport reactors.

- (a) Metal-oxide sorbents with high reactivity/capacity and thermal/mechanical stability/durability will be formulated by the physical mixing method or the impregnation method.
- (b) Experimental procedures will be developed for both sulfidation and regeneration reactions of formulated metal oxide sorbents at high pressures and high temperatures.
- (c) Analytical procedures will be developed for the analysis of concentrations of both sulfur dioxide and hydrogen sulfide in a reaction product gas mixture.
- (d) Thermal/mechanical stability of formulated metal oxide sorbents from cyclic sulfidation/regeneration reactions will be investigated in the isothermal stirred batch reactor or the isothermal continuous differential reactor.

Effects of reaction variables on sulfidation/regeneration reaction kinetics will be investigated for formulated promising metal oxide sorbents. The reaction variables include concentrations of coal gas components, total pressures, reaction temperatures, space velocities of gases for continuous differential reactor operations, initial mass ratios of coal gases to sorbents for batch reactor operation operations, particle sizes of sorbents, and pore volumes of sorbents.

- (a) Effects of concentrations of coal gas components such as hydrogen, nitrogen, oxygen, carbon monoxide, carbon dioxide, and moisture on both sulfidation and regeneration reaction kinetics will be evaluated at various reaction temperatures and pressures, using a stirred batch reactor.
- (b) Effects of total pressures and reaction temperatures on sulfidation/regeneration reaction kinetics for formulated metal oxide sorbents will be determined in a stirred batch reactor or a continuous differential reactor.



- (c) Roles of initial mass ratios of sorbents to sulfidation/regeneration gas mixtures, particle sizes of sorbents, and pore volumes of sorbents will be found, using a stirred batch reaction system.
- (d) Roles of space velocities of regeneration gas mixtures, and particle sizes of sorbents, pore volumes of sorbents will be delineated, using a continuous differential reaction system.

## EXPERIMENTAL APPROACH

The main objectives of this project are to investigate reaction kinetics on the removal of sulfur compounds from coal gases at high temperatures and high pressures, using promising solid metal oxide sorbents, to study kinetics on the regeneration of sulfided sorbents, and to formulate promising durable metal oxide sorbents of high-sulfur-absorbing capacity.

During the first year, fresh metal oxide sorbent particles with promising formulas and simulated coal gases containing hydrogen sulfide are introduced in a batch reactor. The batch reactor, loaded with the fresh sorbent and the simulated coal gas mixture, is submerged in a fluidized sand bath to maintain the heterogeneous reaction system at a desired reaction temperature. Fine metal oxide sorbents will be used to minimize effects of intraparticle diffusion of hydrogen sulfide through sulfided sorbent particles. The batch reactor, loaded with a mixture of fresh sorbent and simulated coal gas mixtures, is shaken in a constant-temperature fluidized sand bath to reduce effects of mass transfer of hydrogen sulfide to sorbent particles. The sulfidation reaction is terminated at the desired reaction time. Conversions of sorbents are analyzed with an electronic balance and a gas chromatograph.

Experiments on the regeneration of sulfided sorbents will be conducted in the batch reactor. Effects of regeneration temperatures, regeneration pressures, and concentrations of regeneration gases such as oxygen, nitrogen, and moisture on regeneration rate will be investigated in the batch reactor.

Precise laboratory procedures will be developed for H<sub>2</sub>S-sorbent heterogeneous reactions in a batch reactor at high pressures and high temperatures. This will involve developing procedures for the proper set-up of a batch reactor and a gas chromatograph for the reaction system. Experiments on intrinsic initial reaction kinetics as well as regeneration kinetics will be performed for the metal-oxide sorbents-H<sub>2</sub>S heterogeneous reaction system. Known amounts of carbon disulfide aqueous solution of various concentrations as a hydrogen sulfide feed stock will be introduced in the batch reactor. Carbon disulfide is decomposed in the presence of hydrogen to produce hydrogen sulfide at precise desired quantities. Known amounts of hydrogen peroxide aqueous solution of various concentrations, as an oxygen feedstock, will be fed into the batch reactor.

## STATUS OF THIS RESEARCH PROJECT

Research activities and efforts of this research project were concentrated on setting up and testing the recently-purchased new instruments such as a gas chromatograph, a pressure transducer, and a pressure meter, and the existing fluidized sand bath and its temperature controller as well as the existing shaker for a batch reactor, fabricating a batch reactor (see Figure 1), and investigating conversions of carbon disulfide in the presence of water and nitrogen in the fabricated batch reactor at elevated temperatures (see Tables 1 and 2).

The gas chromatograph is equipped with a flame photometric detector (FPD) and a thermal conductivity detector (TCD). Sulfur compounds such as  $\text{H}_2\text{S}$  and  $\text{SO}_2$  are analyzed with the FPD detector, using a Super Q column. Nitrogen, oxygen, hydrogen and water are analyzed with the TCD detector, using a HaySep A column.

Conversions of carbon disulfide increase with reaction temperatures. Conversions of carbon disulfide appear to be insignificant below  $350^\circ\text{C}$ , whereas conversions of carbon disulfide appear to be very significant above  $400^\circ\text{C}$ . The 316 stainless steel (SS) batch reactor itself was reacted with hydrogen sulfide, which was not detected by the flame photometric detector (FPD).

The batch reactor was fabricated with Cajon fittings, which do not provide tight sealing for batch reaction experiments during quenching reactions. The batch reactor, equipped with Cajon fittings, appear to be unsuitable for cycled experiments such as sulfidation and regeneration.

## PLANS ON FUTURE EXPERIMENTS

A new batch reactor will be fabricated with Swagelok fittings, and then the fabricated reactor will be alonized (aluminum oxide treated) to prevent reacting the 316 SS reactor itself with hydrogen sulfide. Reactivities of carbon disulfide in the presence of steam and nitrogen will be investigated for the possible source of hydrogen sulfide for this research.

Hydrogen peroxide will be used as a source of oxygen for the regeneration of sulfur-loaded sorbents. Decomposition of hydrogen peroxide in the presence of steam and nitrogen will be investigated in a batch reactor. Initial reaction kinetics on both sulfidation of sulfur-free sorbents and regeneration of sulfided sorbents will be conducted with the ZT-4 sorbent from the Research Triangle Institute.

Table 1. Reaction conditions on conversion of carbon disulfide into hydrogen sulfide.

|  |           |
|--|-----------|
| Reactor Volume, cm <sup>3</sup> :      | 13        |
| Temperature, °C:                       | 300 - 600 |
| Total Pressure, psia:                  | 200 - 500 |
| Reaction Time, min:                    | 10        |
| Initial Amount of CS <sub>2</sub> , g: | 0.002     |
| Initial Amount of Water, g:            | 0.004     |
| Initial Nitrogen Pressure, psig:       | 150       |

Table 2. Conversion of carbon disulfide into hydrogen sulfide at various temperatures.

| Temperature, °C | Conversion, % |
|-----------------|---------------|
| 300             | 0             |
| 350             | 6             |
| 400             | 73            |
| 450             | 81            |
| 500             | 93            |
| 550             | 96            |

Figure 1. A SCHEMATIC DIAGRAM ON A BATCH REACTOR

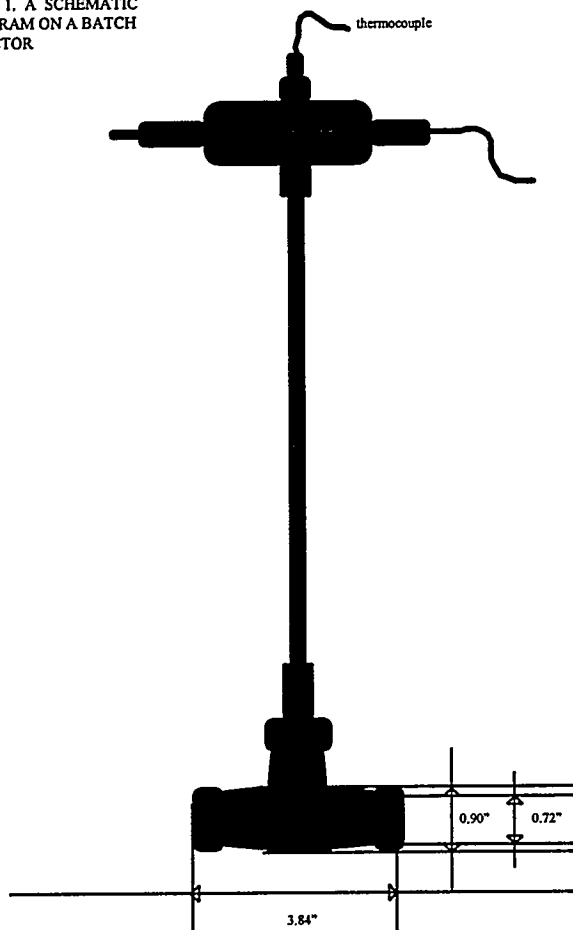


Figure 2. Conversion of Carbon Disulfide

