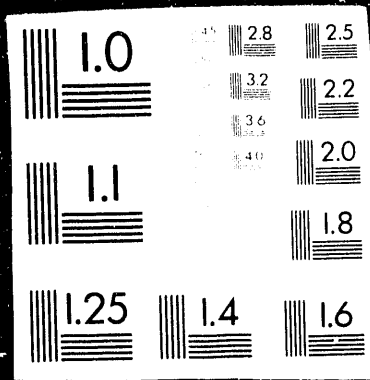


0009185

1 OF 1



DIRECT METHANE CONVERSION TO METHANOL

Project Status Report - Quarterly

(07/01/92 -- 09/30/92)

John L. Falconer and Richard D. Noble

Department of Chemical Engineering
University of Colorado
Boulder, CO 80309-0424

DOE/MC/27115--3280

DE93 009183

Prepared for

U.S. Department of Energy

Morgantown Energy Technology Center
Contract No. DE-FG21_90MC27115

DISCLAIMER

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States DOE, nor any of their employees, nor any of their contractors, subcontractors, or their employees makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED *CP*

DIRECT CATALYTIC CONVERSION OF CH₄ TO CH₃OH IN A NON- ISOTHERMAL MEMBRANE REACTOR

PROJECT STATUS REPORT -- QUARTERLY

(07/01/92 -- 09/30/92)

PROJECT DESCRIPTION

We proposed to demonstrate the effectiveness of a catalytic membrane reactor (a ceramic membrane combined with a catalyst) to selectively produce methanol by partial oxidation of methane. Methanol is used as a chemical feedstock, gasoline additive, and turbine fuel. Methane partial oxidation using a catalytic membrane reactor has been determined as one of the promising approaches for methanol synthesis from methane. In the original proposal, the membrane was assumed to be used to selectively remove methanol from the reaction zone before carbon oxides form, thus increasing the methanol yield. Methanol synthesis and separation in one step would also make methane more valuable for producing chemicals and fuels.

CURRENT SITUATION

Many membranes were tested in a high pressure system, but none of them could selectively remove methanol at the high pressure and temperature necessary for methanol formation. As an alternate approach, a cooling tube was inserted inside the membrane reactor to create a low temperature zone that rapidly quenches the product stream. This system has proved effective for increasing methanol selectivity during CH₄ oxidation, and we are using and modifying this non-isothermal, non-permeable membrane reactor.

PROGRESS

Analysis of previous results showed that CH_3OH selectivity when rapid quenching is used is double that obtained without rapid quenching (Fig. 1, 2). For both conditions, the combined selectivity for CH_3OH and CO is constant (about 85%) (Fig. 3). The remaining product is CO_2 . When the product stream was quenched, further oxidation of CH_3OH to CO was inhibited and more CH_3OH molecules were obtained in the exit stream.

The membranes were broken when removed from the system, apparently because of the large radial thermal gradient in the reactor. During an experiment, the outer surface of the ceramic membrane was hot because of heating by the furnace while the inner surface of the membrane was cool because of the cooling tube, which was very close to the membrane. The original cooling tube was replaced by one with a smaller diameter, and the most experiments indicate the membrane is intact.

In the previous experiments, only the reactor wall temperatures were measured. For better understanding of the process, the temperatures inside the reactor, especially inside of the catalyst bed need to be measured. Two thermocouples were added to the system to measure the temperatures of the catalyst bed (Fig. 5) and exit cooling water from the cooling tube.

Much of the time this quarter was spent analyzing the results and writing a draft of a paper describing the improvements obtained with the membrane reactor. Though additional experiments are still required, the analysis has indicated the direction for future experiments. A poster on this work was prepared for presentation at the Annual AIChE meeting in Miami.

WORK PLANNED FOR CURRENT QUARTER

1. Change the length of the membrane for adjusting the resident time;
2. Systematic experiments to find optimal operating conditions (temperature, pressure, resident time).

Since the mass flow controllers in this system have a maximum flow rate of 500 sccm, short residence time can not be obtained unless a small volume of catalyst is used. A viable way

to change the catalyst bed volume is to change the membrane length. A membrane with a shorter length has been prepared.

Because the cooling tube and the membrane have been changed, it is necessary to repeat the previous experiments to see how those changes affect the selectivity and conversion. Systematic studies will then be carried out to find the optimal operating conditions.

CH₃OH Selectivity Increased by Rapid Quenching

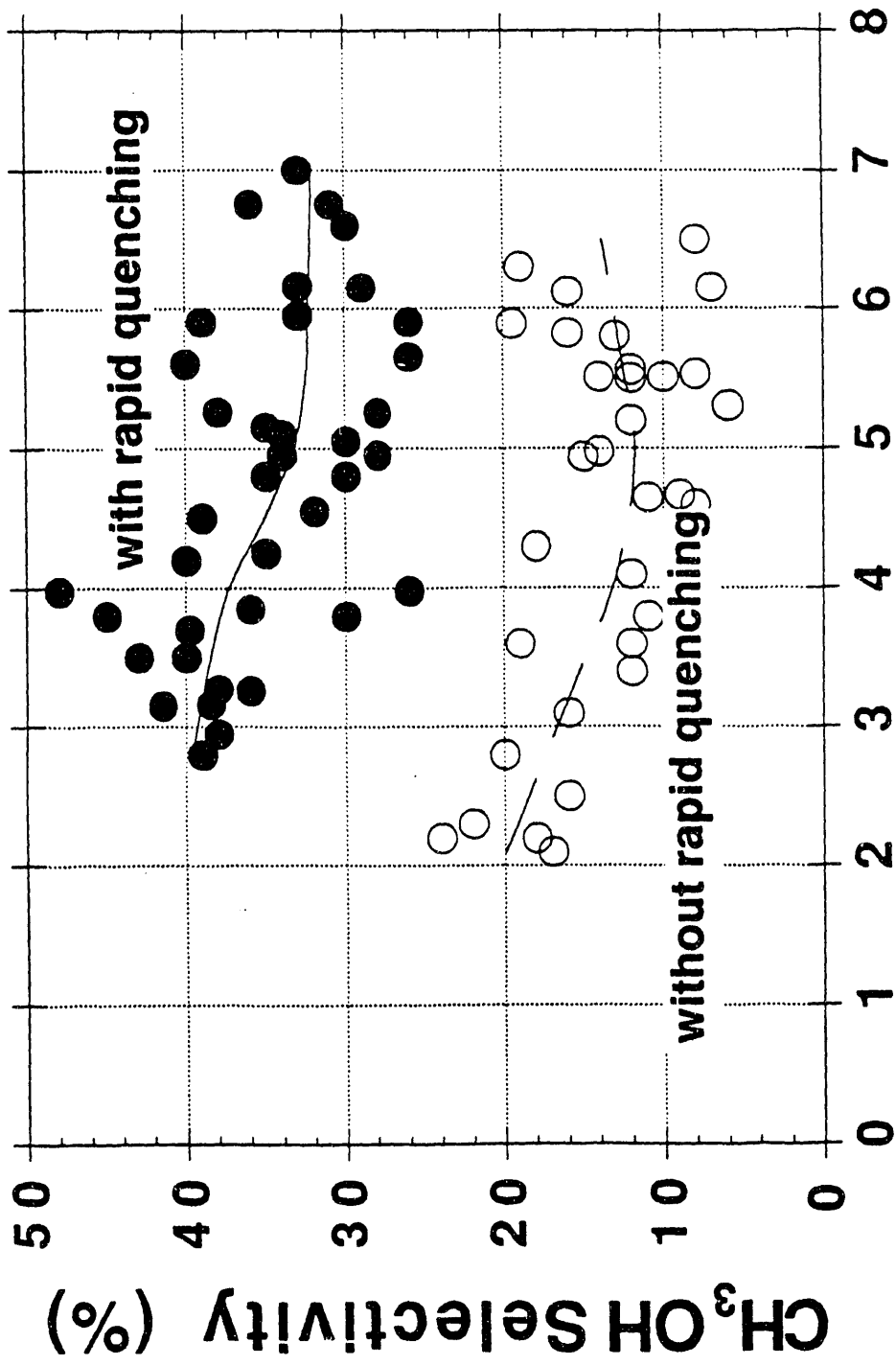


Fig. 1 CH₄ Conversion (%)

CH₃OH Selectivity Increased by Rapid Quenching

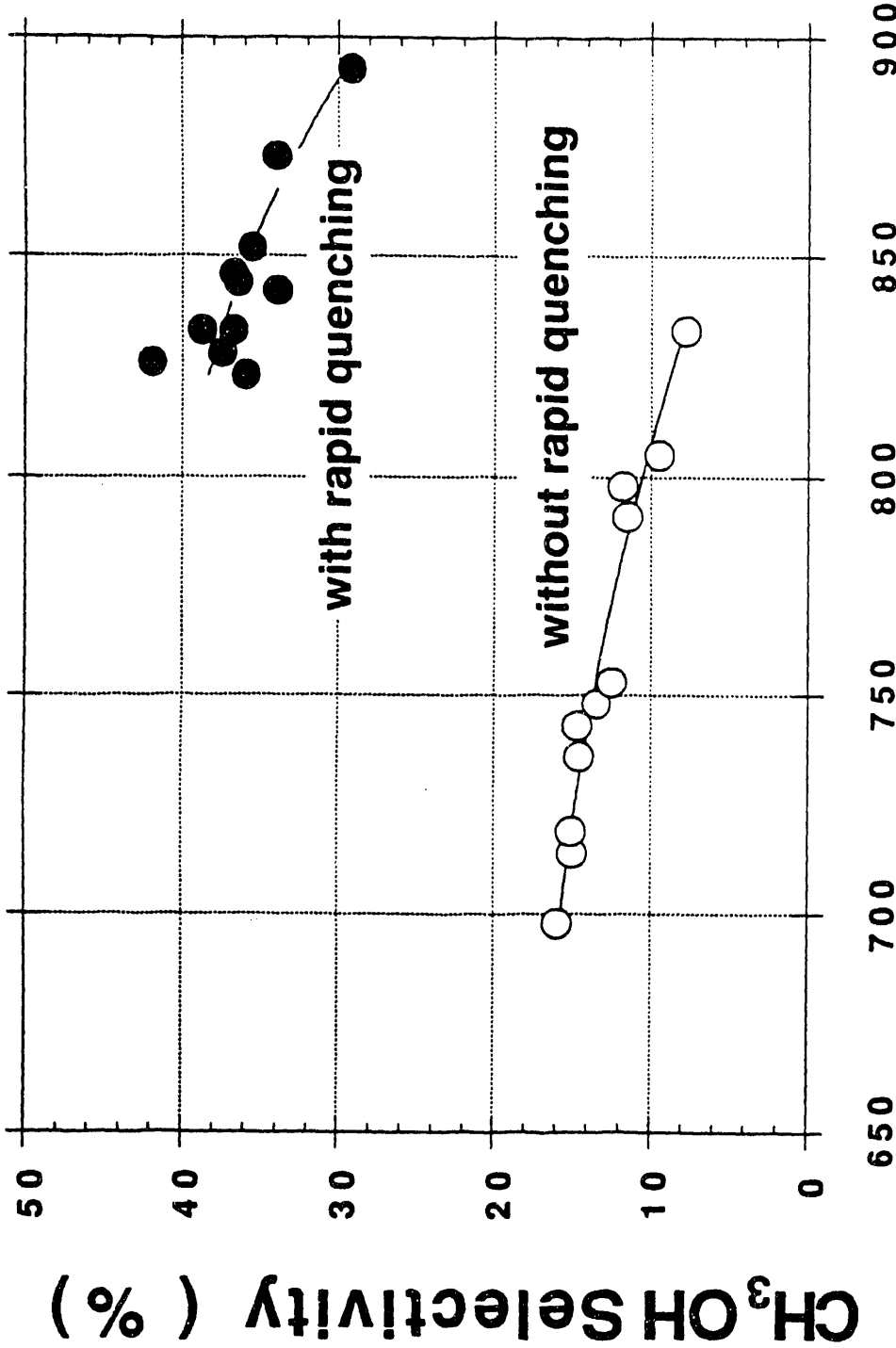


Fig. 2 Temperature (K)

Constant $\text{CH}_3\text{OH} + \text{CO}$ Selectivity

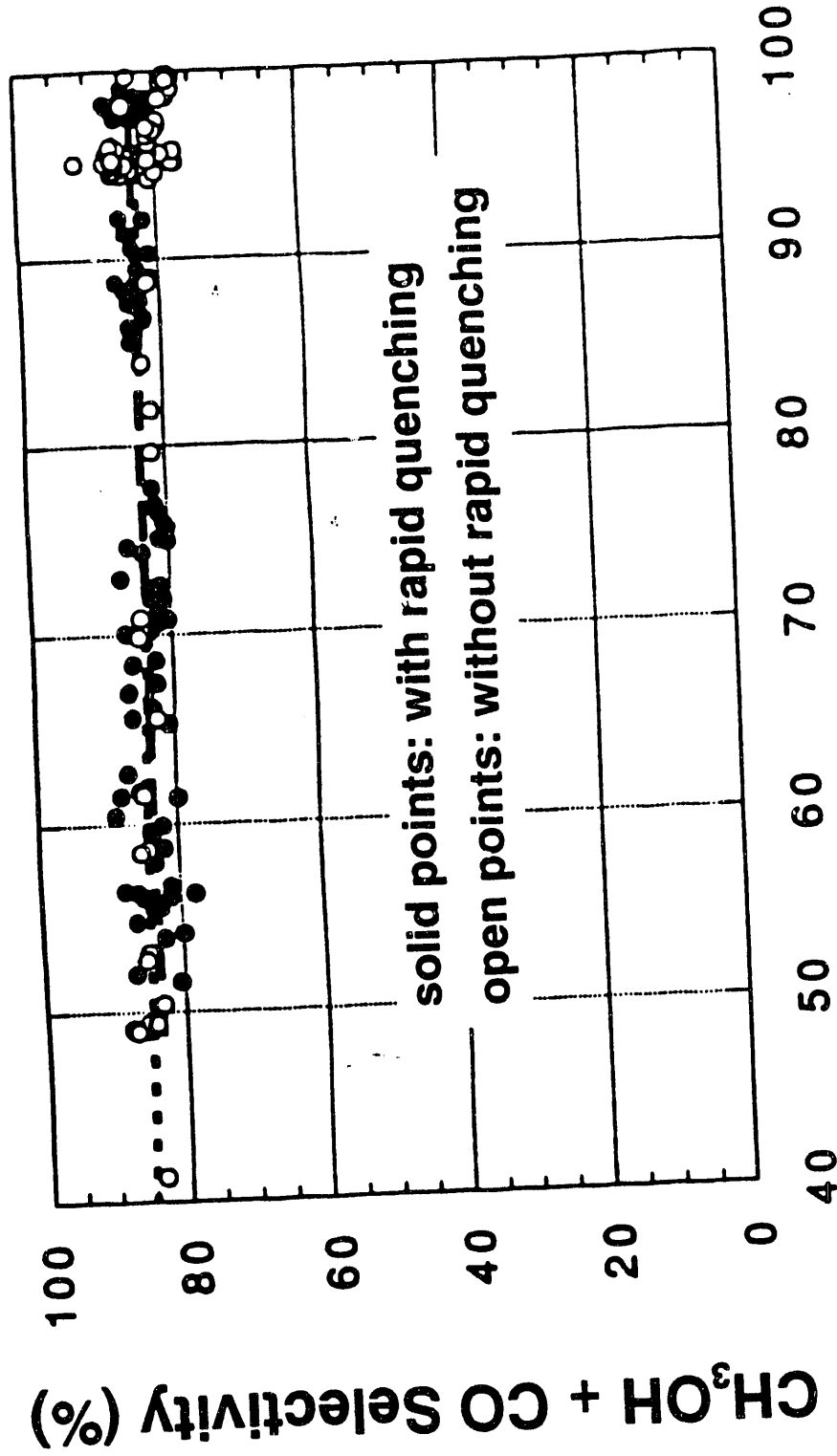


Fig. 3 O_2 Consumption (%)

Decreased CO Is Increased CH_3OH

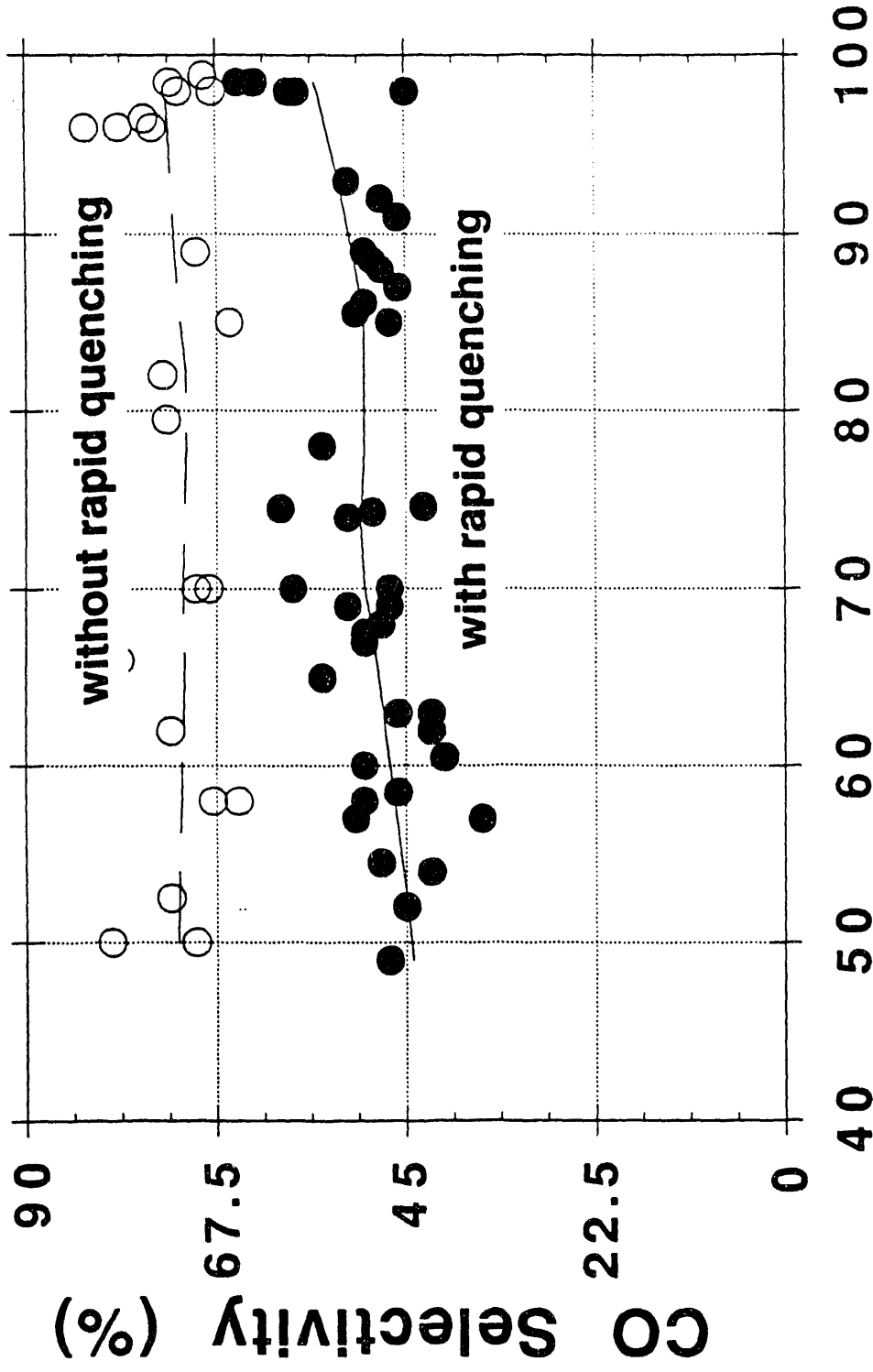
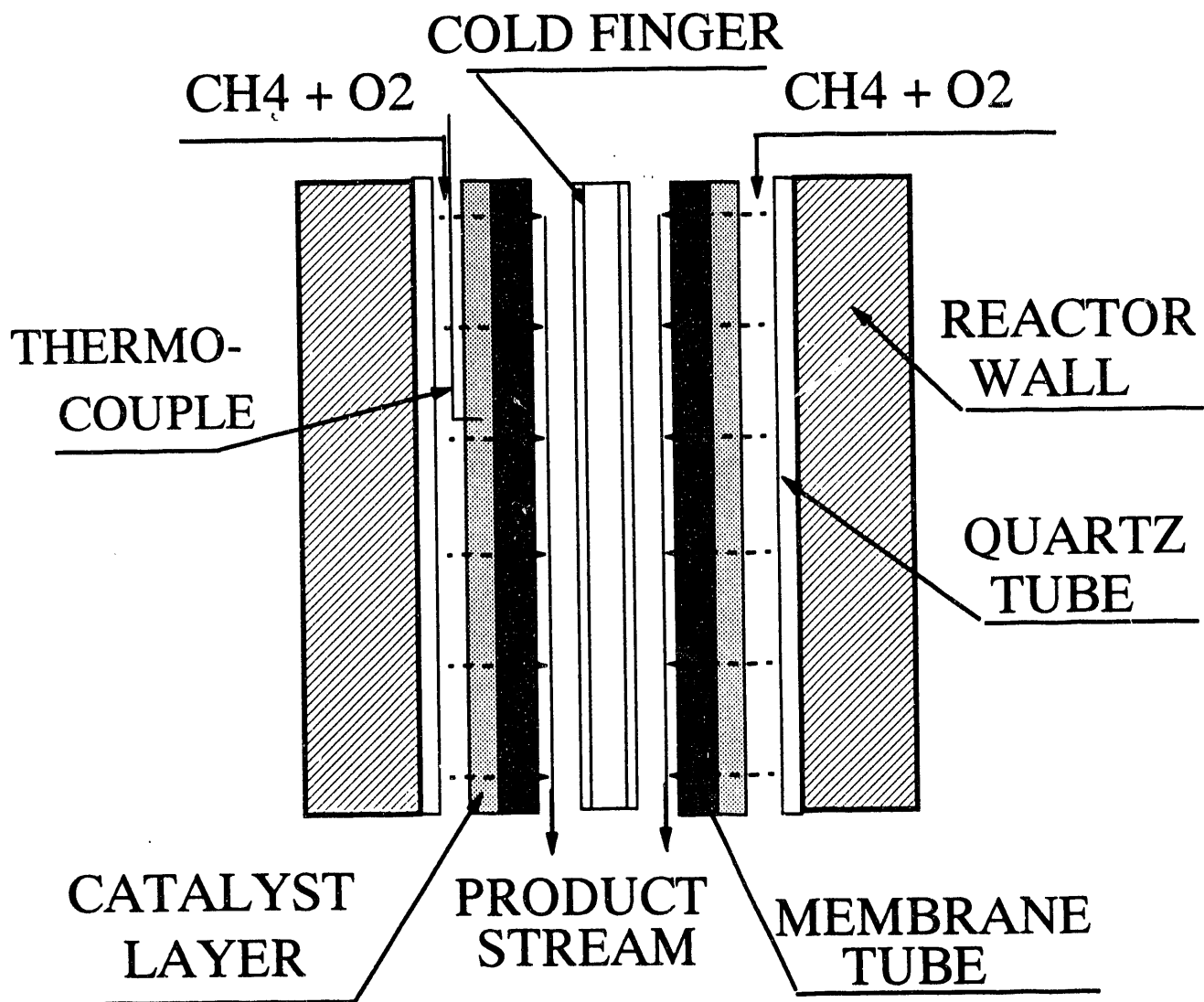


Fig. 4 O₂ Consumption (%)

Fig. 5

REACTOR DETAIL

(MEMBRANE SECTION)



END

**DATE
FILMED**

4 / 7 / 93

