DEPARTMENT OF ENERGY

DOE/PC/92529--T14

Quarterly Technical Progress Report

Due date Jan. 31, 1995

Period of report 10/1/95 to 12/31//95

Project DE-FG22-92PC92529

Transient Studies of Low Temperature Catalysts for Methane Conversion

directed by

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DISCLAIMER

BRIEF SUMMARY OF PROGRESS

This report summarizes progress made on a new method of producing synthesis gas from methane using a fast flow membrane reactor. Experiments were performed using a Rh catalyst in a traditional fixed bed reactor to provide a comparison to results that will be obtained in the membrane reactor.

SUMMARY OF PROGRESS

We have previously reported that a 3% Rh/TiO_2 catalyst was active for the partial oxidation of methane to synthesis gas at relatively low temperatures. Schmidt and coworkers [1] have shown that high conversions and selectivities to syngas can be achieved on Rh coated monolith catalysts. However, the operation of the reactor requires first igniting the catalyst at temperatures around 600°C using ammonia oxidation. Our catalyst will ignite at around 320°C upon introduction of oxygen into a flowing methane stream, eliminating the need for a pre-reaction ignition.

The problem with the partial oxidation reaction is that the methane/oxygen feed ratio required for adequate results is near the explosive limit. Therefore, a means of removing the explosive hazard was developed. In our previous report we described how a membrane reactor would be used to prevent the potential explosive hazard, see Figure 1. The membrane tube will keep the methane and oxygen separated until they reach the catalyst surface. Because oxygen conversion is near 100%, there is no possibility that explosive limits could be reached in this configuration.

Before performing extensive experiments with the membrane reactor, it was decided to conduct a full study of the reaction using the catalyst in a traditional fixed bed reactor. This would allow for a means of comparison so that the full effect of the membrane reactor could be evaluated. Three separate studies were conducted.

Figure 2 shows the effect of the total feed rate on the partial oxidation reaction. In these experiments, 30 mg of catalyst were used, and the methane/oxygen feed ratio was held constant at 2/1. As the flow rate increased both methane conversion and CO selectivity increased to around 70% and 90% respectively. Hydrogen selectivity reached a maximum of around 75% between 600 and 800 cc/min. At the higher flowrates, more heat was evolved and it would appear that the higher temperatures corresponded to a larger amount of water being formed, and thus a smaller amount of hydrogen.

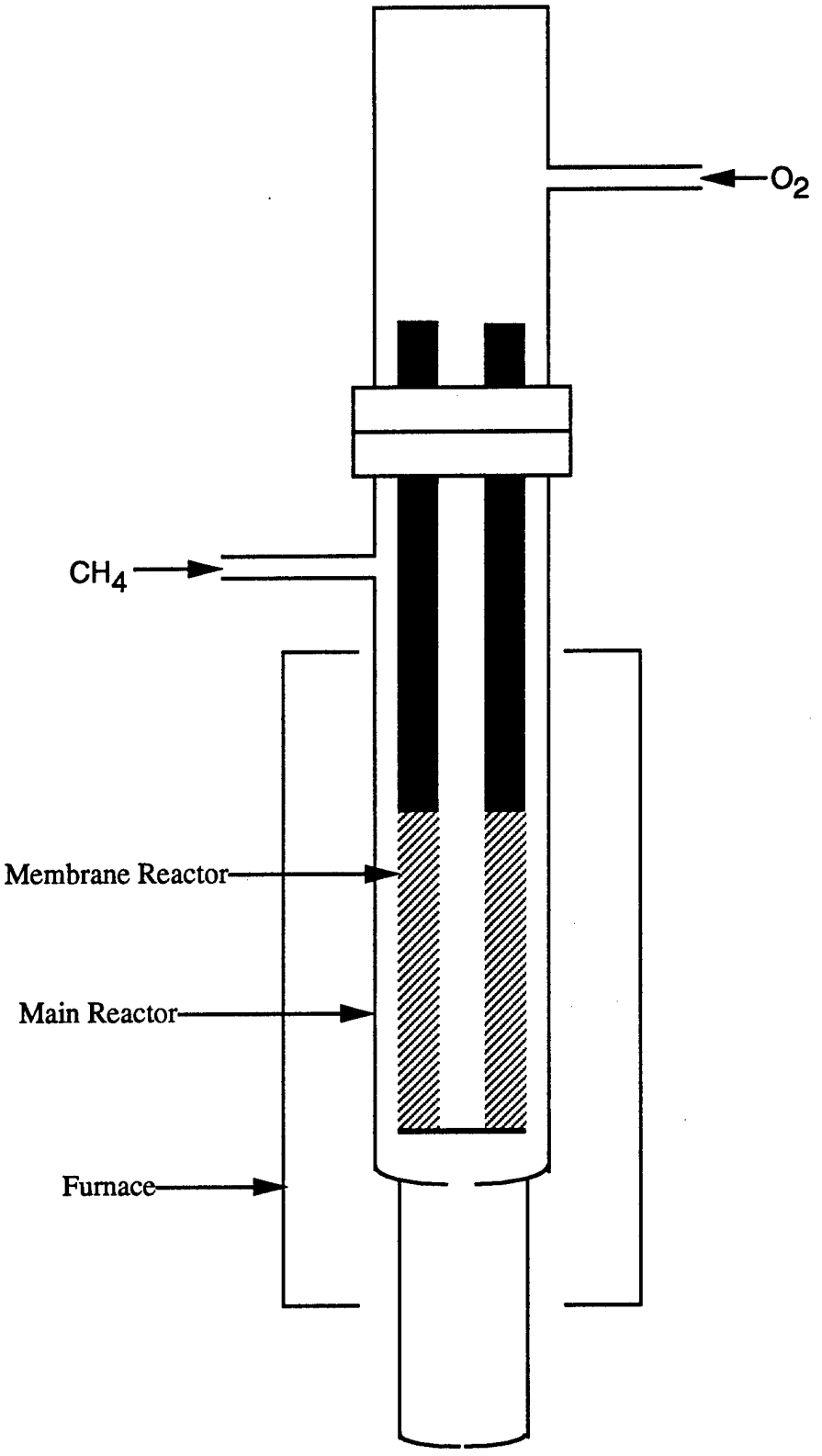
Figure 3 shows the effect of catalyst loading on syngas production. In these experiments the feed rates of methane and oxygen were maintained at 500 and 250 cc/min respectively. The general trend is that conversions and selectivities increase and reach an optimum value at around 40 mg of catalyst. At this value H_2 and CO selectivities above 90% have been achieved with a

methane conversion around 70%. As in Figure 2, the oxygen conversion remains constant at nearly 100% conversion.

Figure 4 shows the results of varying the methane/oxygen feed ratio. In this set of experiments, 30 mg of catalyst were used. No experiments were performed in which the feed ratio was significantly below 2/1 due to the fact that such operation would occur well within the explosive region. Except for a drop in methane conversion, varying the feed rate in this region did not appear to significantly alter the results. CO selectivity remained close to 90%, H_2 selectivity around 75%, and oxygen achieved close to 100% conversion. To fully determine the effect of the feed ratio, a wider range must be tested, but this can be accomplished only in the membrane reactor.

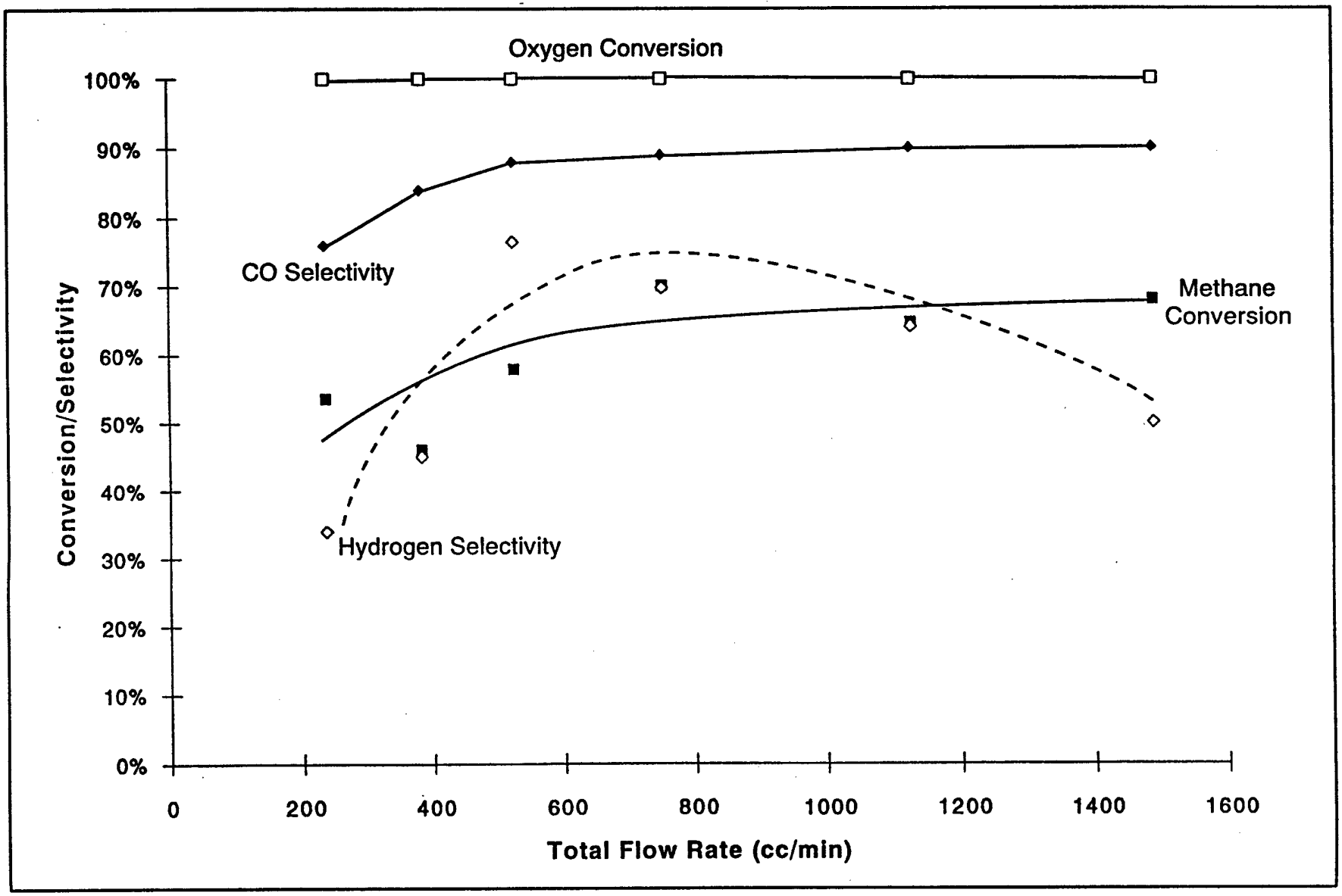
The next step in the project will be to fully implement the membrane reactor. The external quartz reactor has been procured, and the membrane tube has been sealed and glazed. Experiments similar to the fixed bed reactor experiments will be conducted using the membrane reactor. In addition, experiments will be conducted at lower methane/oxygen ratios, which would normally exceed explosive limits in a fixed bed reactor.

1. Hickman, D. A., E. A. Haupfear, and L. D. Schmidt. *Catal. Lett.* **17** 23 (1993).

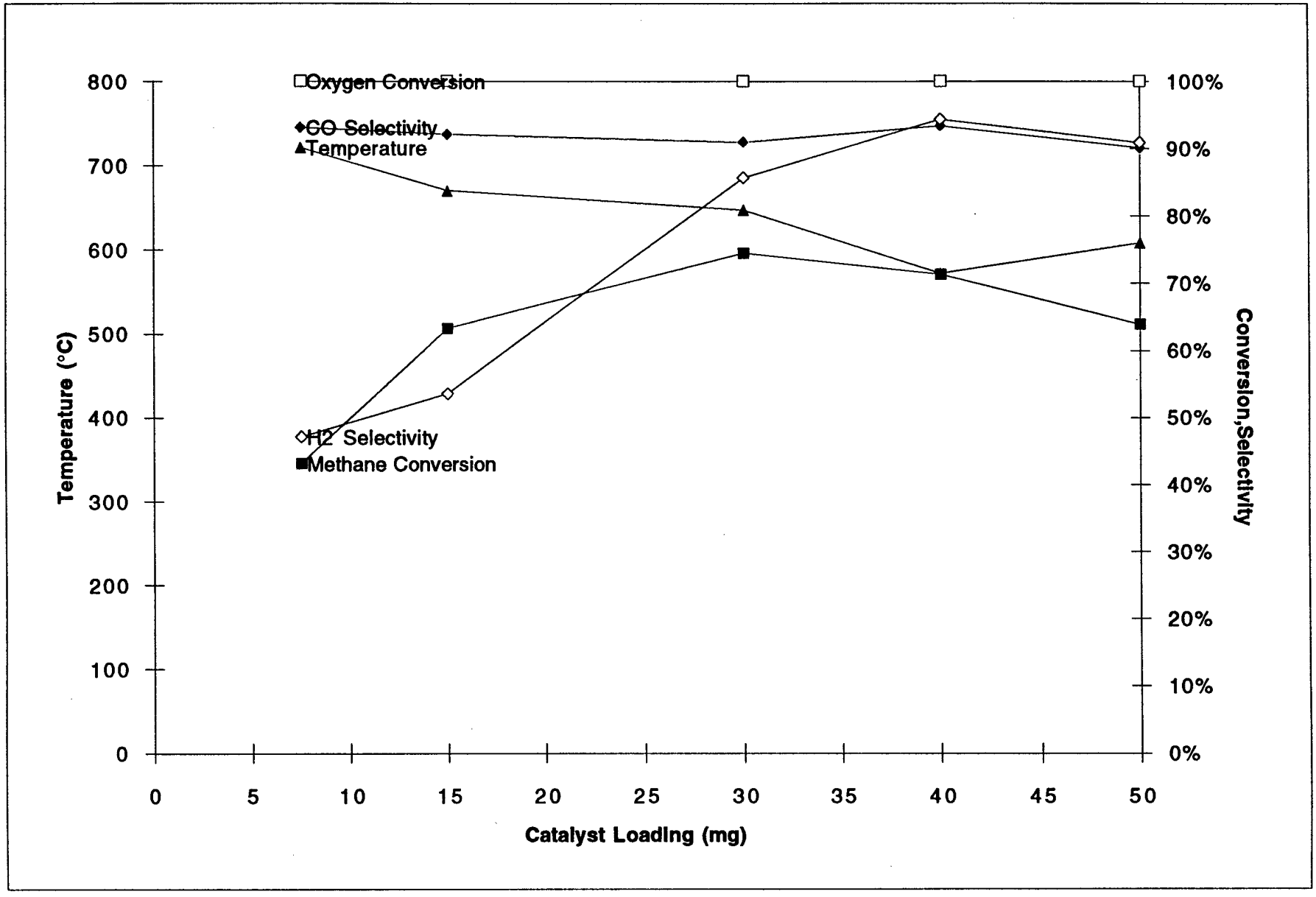

O_2
CH_4
Membrane Reactor
Main Reactor
Furnace

Tig = 330°C

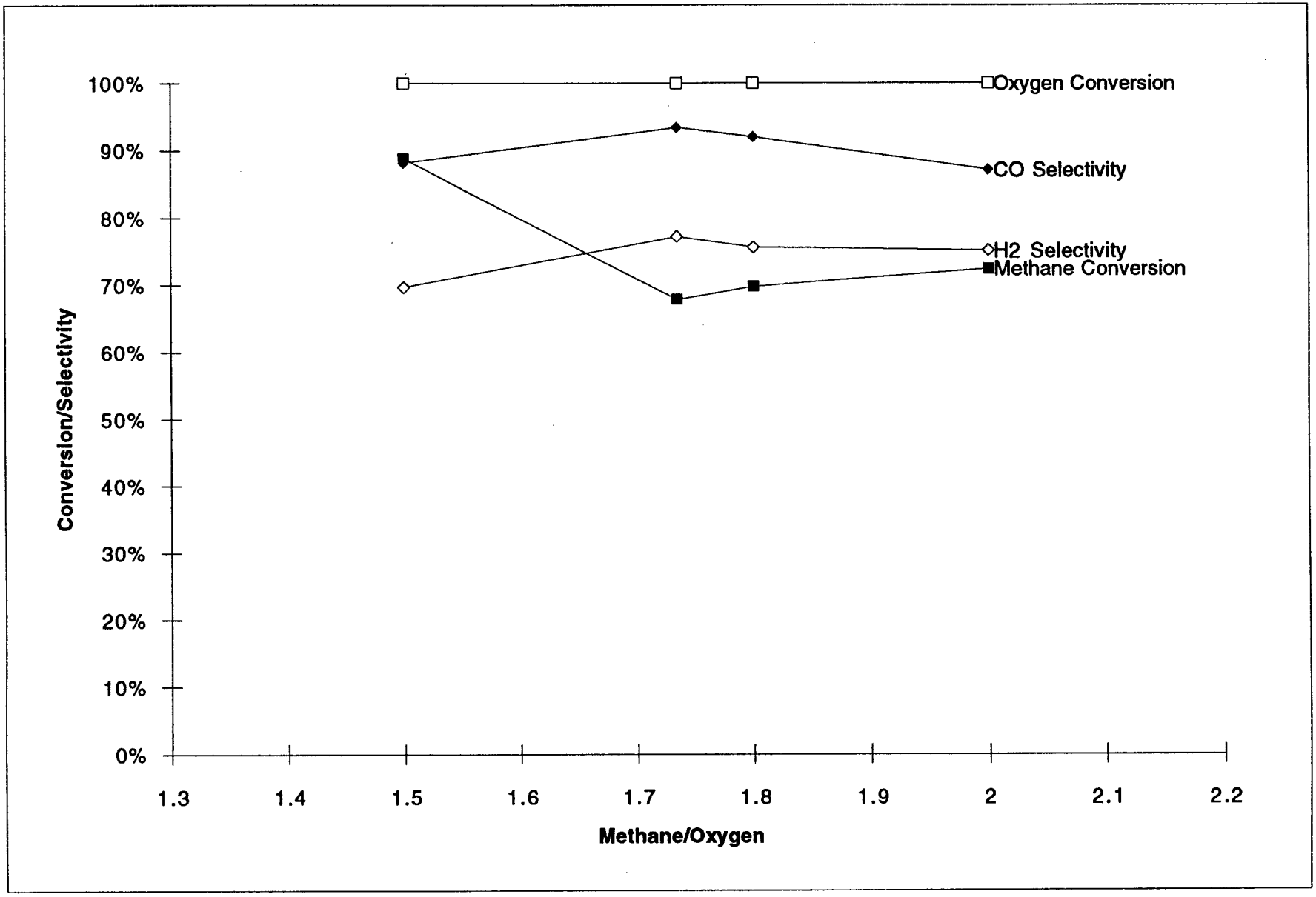
Methane/Oxygen = 2/1



CH4=500 cc/min; O2=250 cc/min Tig=330°C



Tig ≈ 330°C


100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
Conversion/Selectivity
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2
2.1
2.2
Methane/Oxygen
Oxygen Conversion
CO Selectivity
H2 Selectivity
Methane Conversion

Report Number (14) DOE/PC/92529--T14

Publ. Date (11) [199604]

Sponsor Code (18) DOE, XF

JC Category (19) UC-900, DOE/ER

DOE