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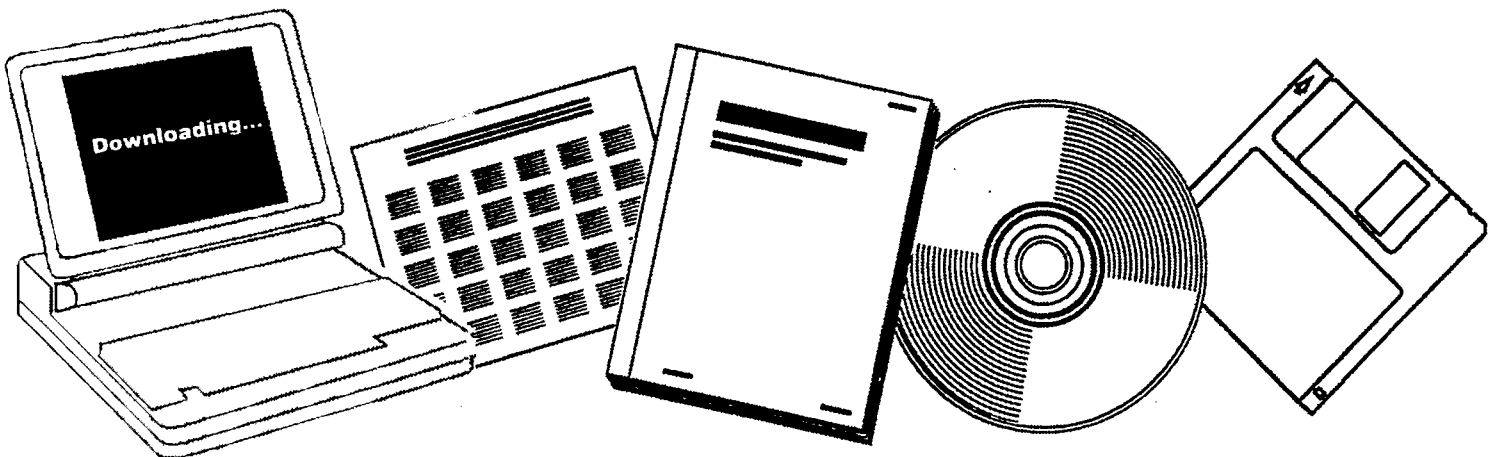
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**CONVERSION OF LOW H SUB 2 /CO RATIO
SYNTHESIS GAS TO HYDROCARBONS. PROGRESS
REPORT, OCTOBER 1-DECEMBER 31, 1982**

**CALIFORNIA UNIV., BERKELEY. DEPT. OF
CHEMICAL ENGINEERING**

1982



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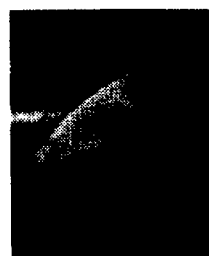
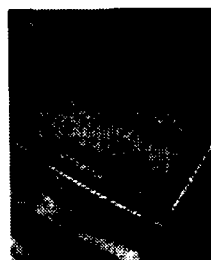
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MASTER

Conversion of Low H₂/CO Ratio Synthesis
Gas to Hydrocarbons

Grant No. DE-FG22-81PC40795

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Progress Report
for the Period

October 1, 1981 to April 1, 1982

Submitted by
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ABSTRACT

The first goals of this project are: 1) to understand the influence of mass transfer on the performance of Fischer-Tropsch slurry reactors, and 2) to determine the nature of carbon formed during reaction. In reaching this second goal, knowledge of the catalyst composition will be useful.

Experiments aimed at the understanding of mass transfer effects have been initiated and the first of these is discussed in this report. It is too early to draw definitive conclusions.

After completion of the experiments on mass transfer, a determination of the rate of free carbon formation in the slurry reactor will be undertaken. The slurry will be analyzed for carbon, iron, and oxygen, via elemental analysis, and the solids will be analyzed by x-ray diffraction. This should allow us to determine the composition of the catalyst and the extent to which free carbon is formed during reaction, and may improve our understanding of the differences between the fixed bed reactor and the slurry reactor.

Another potential set of experiments involves the use of solvents that exhibit varying degrees of miscibility with Fischer-Tropsch products. If deactivation occurs via coke formation from Fischer-Tropsch products, changing the miscibility of products in the slurry will change the rate of catalyst deactivation.

Finally, it is proposed to study Fischer-Tropsch reactions with catalysts in which the active materials are deposited in the pores of a zeolite which are too small to permit coke formation. The exterior surface of the zeolite can be poisoned for acid catalyzed reactions. This will determine whether catalyst deactivation occurs primarily via accumulation of graphitic carbon.

Introduction

The immediate objective of our work remains to understand the mass transfer processes occurring in Fischer-Tropsch slurry reactors. Calculations using mass transfer parameters from the literature lead to the conclusion that mass transfer resistances enhance the hydrogen to carbon monoxide ratio in the slurry phase and that the degree of enhancement depends strongly on the level of conversion in the reactor.

The experiments planned can be divided into two sets. First the reactor is operated at differential conversion, and the weight of catalyst per reactor volume, the carbon monoxide and hydrogen partial pressures, and the temperature are varied. Measuring variation of the reaction rate with weight loading will allow the estimation of mass transfer coefficients, while a kinetic rate expression can be determined from measurements of the reaction rate as a function of T and P. In the second set of experiments, the product distribution will be measured at varying conversion. The results will be compared to calculations based on the rate and mass transfer measurements made in the first set of experiments.

Results

The first of a series of runs at varying catalyst weight loading has been completed. During the run, which lasted 6 days, the effect of temperature on reaction rate and product distribution was examined.

After reduction at 325°C, under 10 atmospheres of hydrogen at 240 NTP cm³/min-g catalyst, reaction started at 300°C, with H₂/CO = 1.0. After about 50 hours, the activity reached a steady value, and the temperature was changed to 270°C. The activity dropped, but over the course of about 18 hours, increased by a factor of two. Figure 1 shows the Schulz-Flory plot for both high and low activity. It can be seen that the chain growth probability did not change as the activity increased. The activity remained steady, and the temperature was lowered to 250°C, where a steady state was achieved within 4 hours. After raising the temperature to 280°C, the activity increased, and, after some fluctuation, reached a slightly lower steady-state value. Returning to 300°C resulted in an activity about 40% higher than the original value. Eventually, after about 24 hours, the activity returned to within 10-15% of its original value. The time-temperature behavior of the activity is shown in Fig. 2. The rate of methane formation is shown as a function of 1/T. At each temperature, the points are numbered in the order in which they were measured. The activation energies for the high and low activities are also shown.

Figure 3 shows Schulz-Flory plots for 300, 270, and 250°C. It can be seen that the chain growth probability remains virtually the same as temperature decreases.

Discussion

The reason for the observed changes in activity is not clear. It is possible that the catalyst is undergoing a reversible change in composition. Madon and Taylor [J. Cat., 69, 32 (1981)] observed changes in catalyst composition with temperature using a precipitated iron catalyst in a fixed bed reactor. As temperature increased, the catalyst changed from Fe_2O_3 and an iron-carbon solution to iron carbide. The change occurred between 240 and 250°C, and was accompanied by an increase in selectivity to C_1 - C_4 hydrocarbons, and a decrease in CO_2 selectivity. They noted that the C_{5+} activity did not change. Figure 4 shows the ratio: CH_4/CO_2 as a function of temperature. The values used are the steady state values at each temperature. The changes observed are not consistent with those observed by Taylor and Madon. Clearly, a better understanding of the observed activity changes requires further work. Determining the catalyst composition as a function of temperature may provide some insights.

The activation energies shown in Fig. 2 indicate that mass transfer is not affecting the rate of the reaction under the conditions studied.

Future Work

The next six months will be devoted to completing the experiments outlined in the introduction. In the next run, the partial pressure dependence of the reaction rate will be studied.

Figure 1

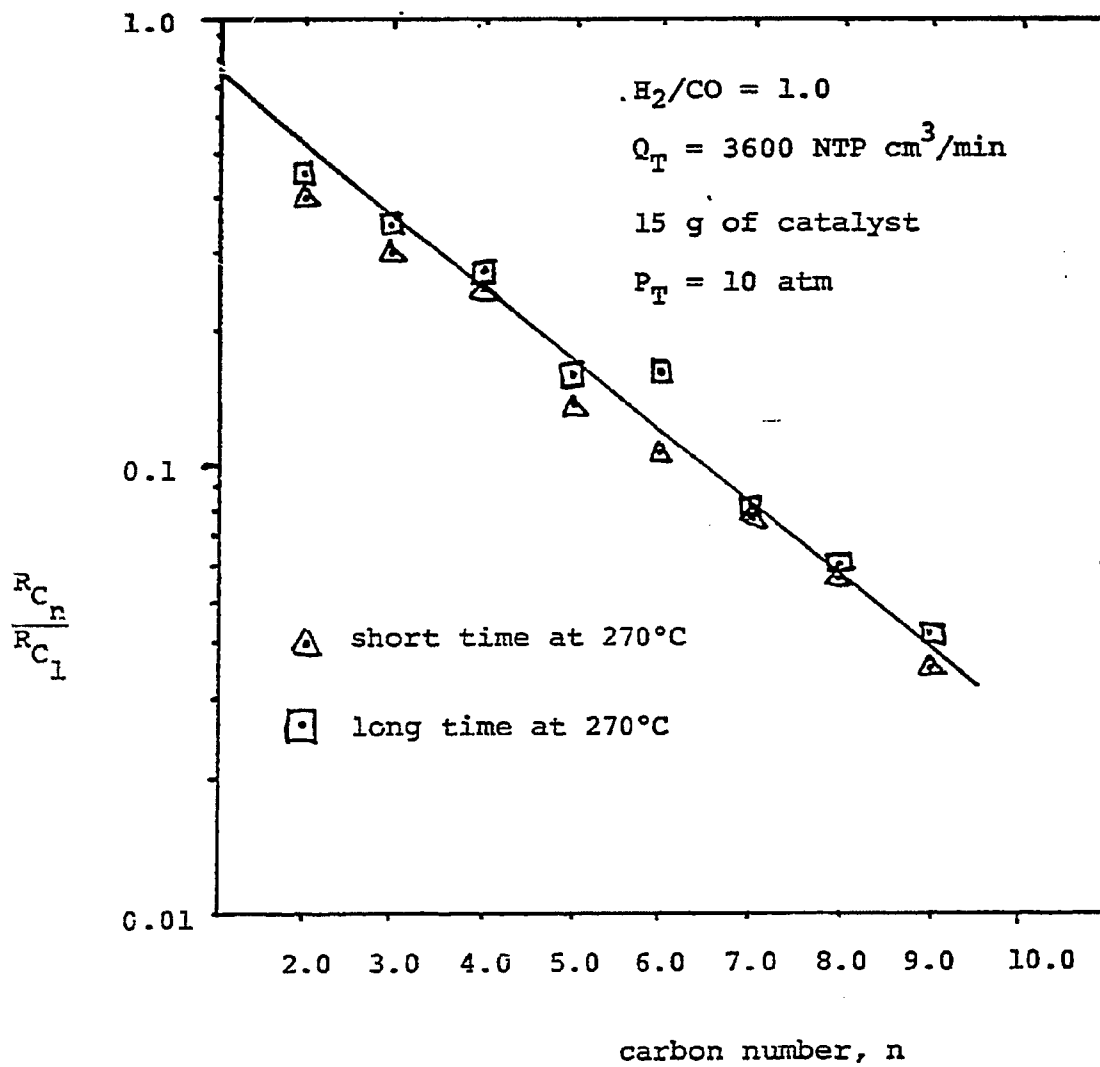


Figure 2

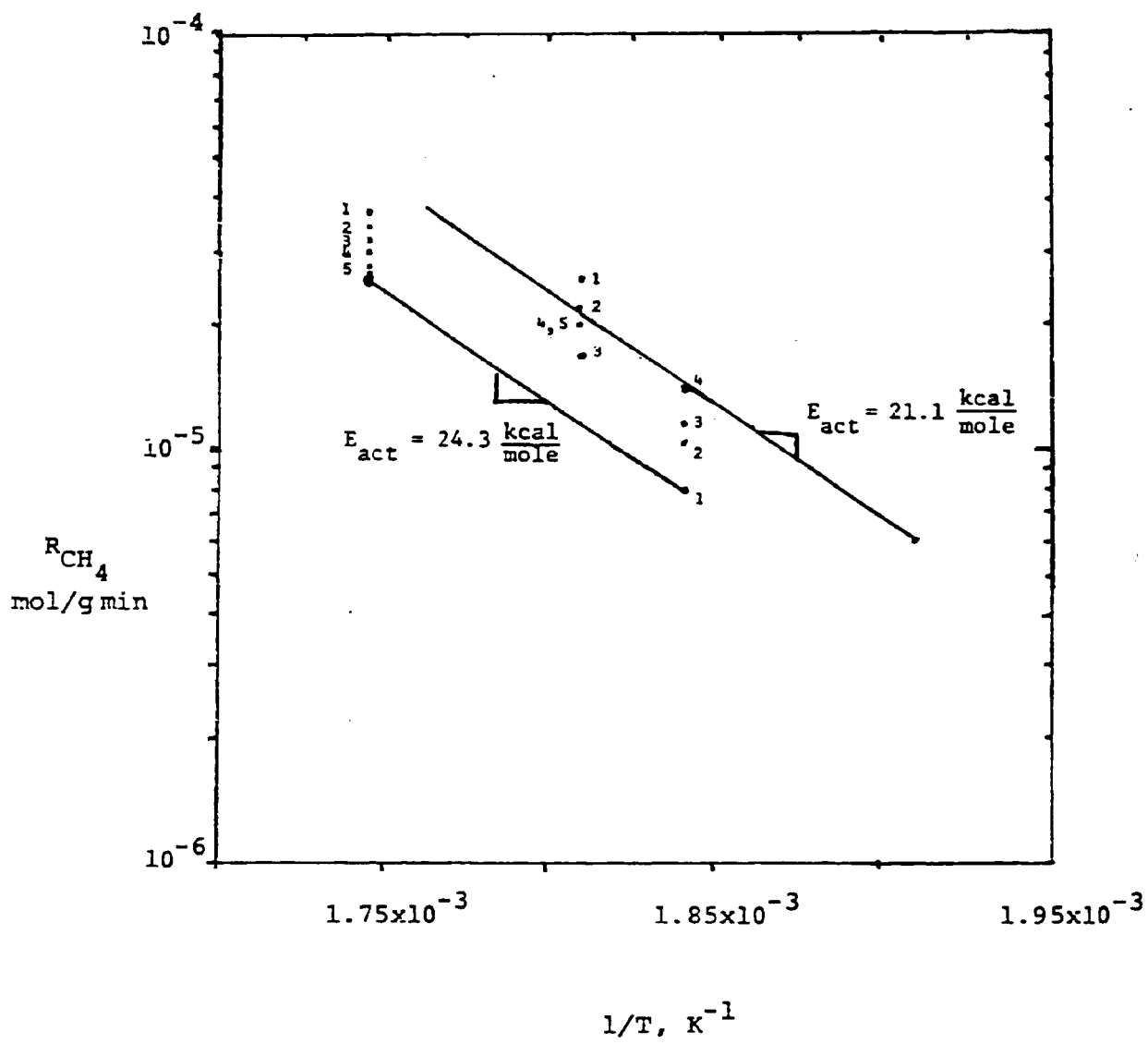


Figure 3

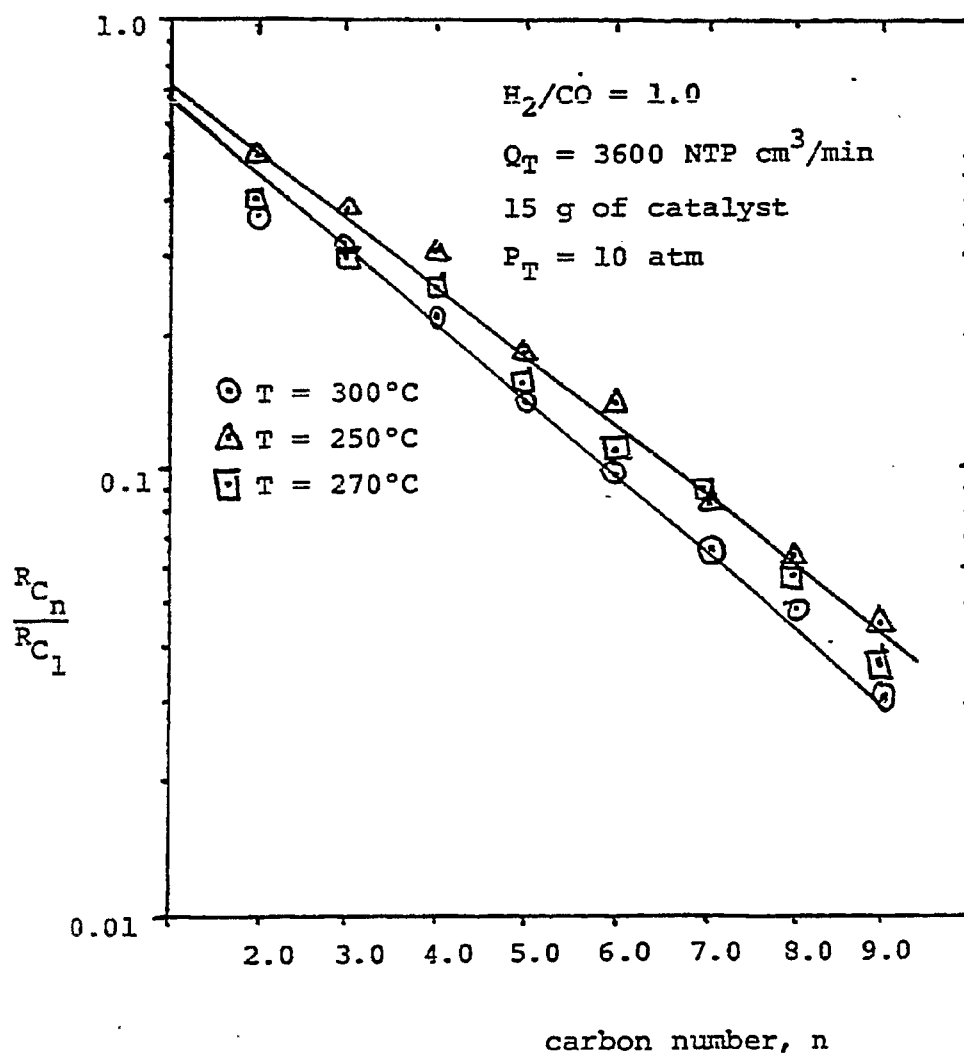
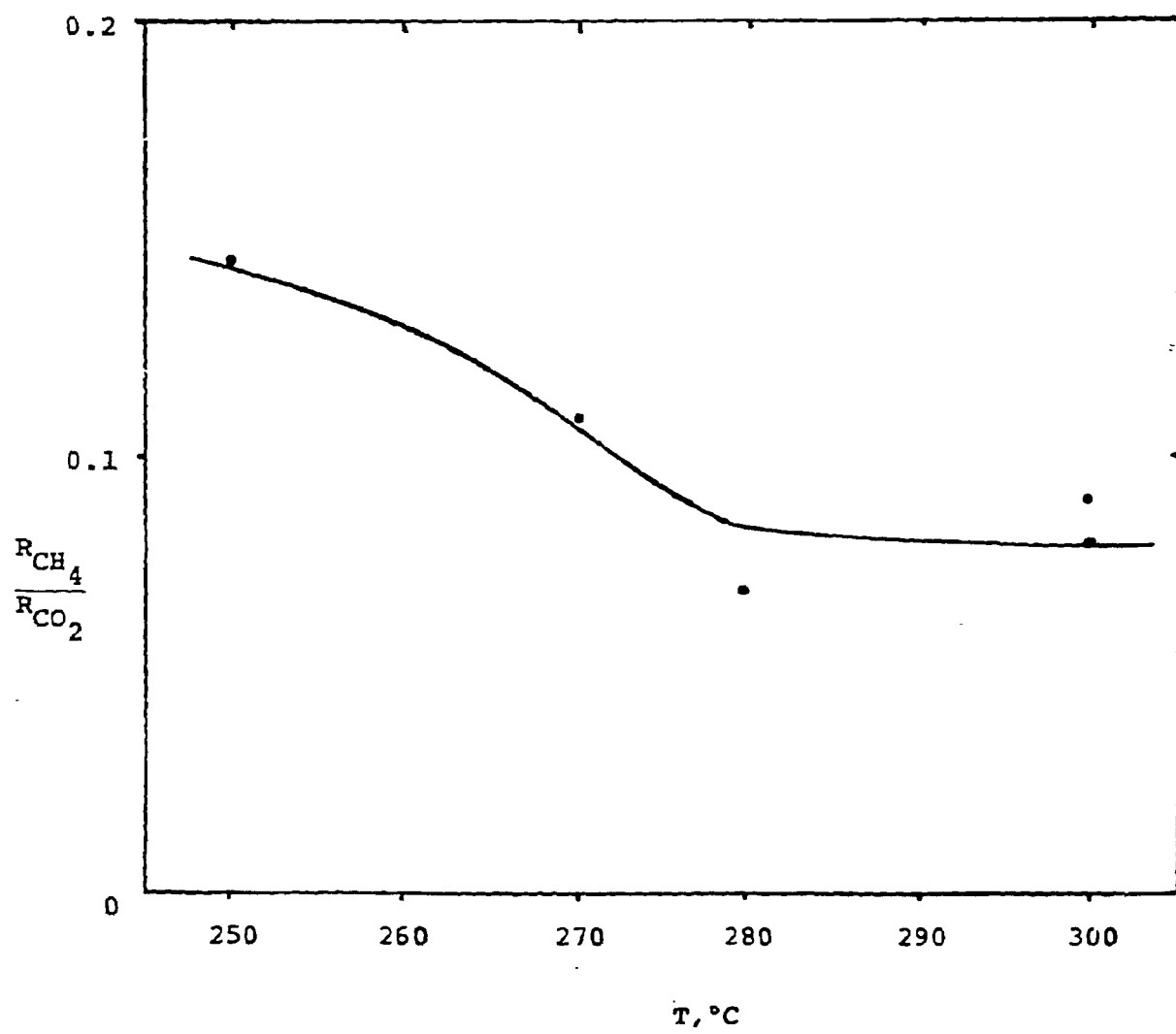


Figure 4



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